

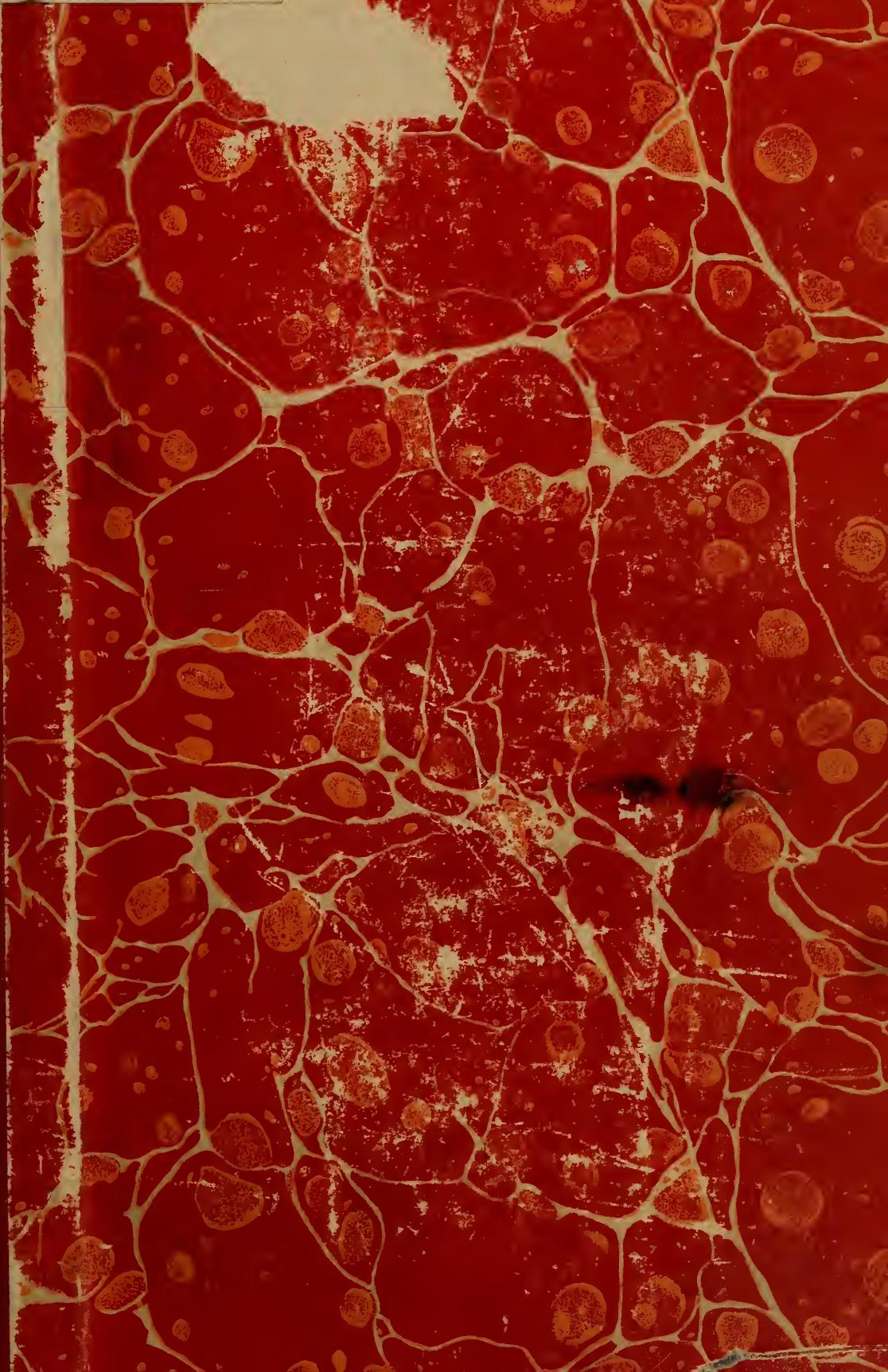
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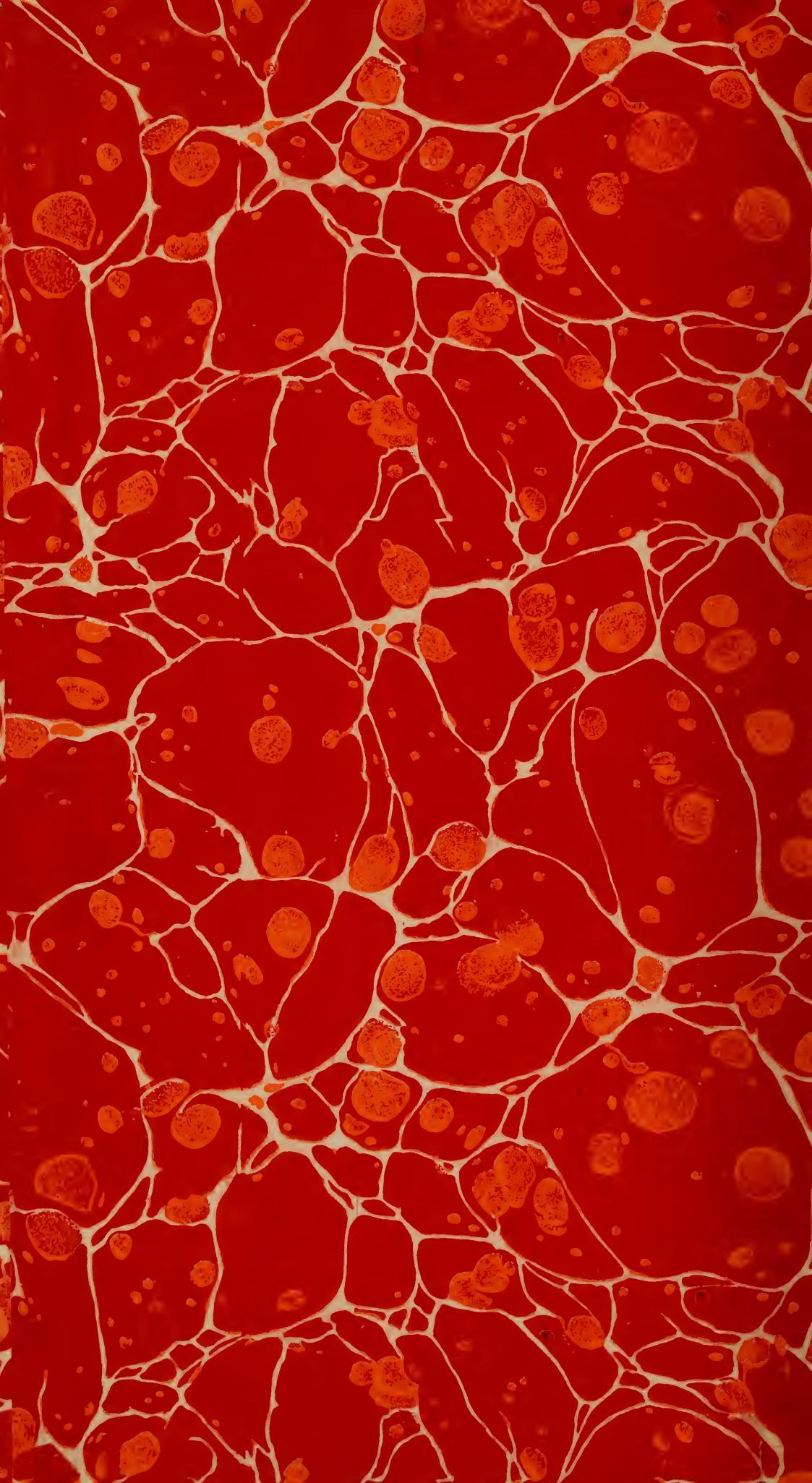
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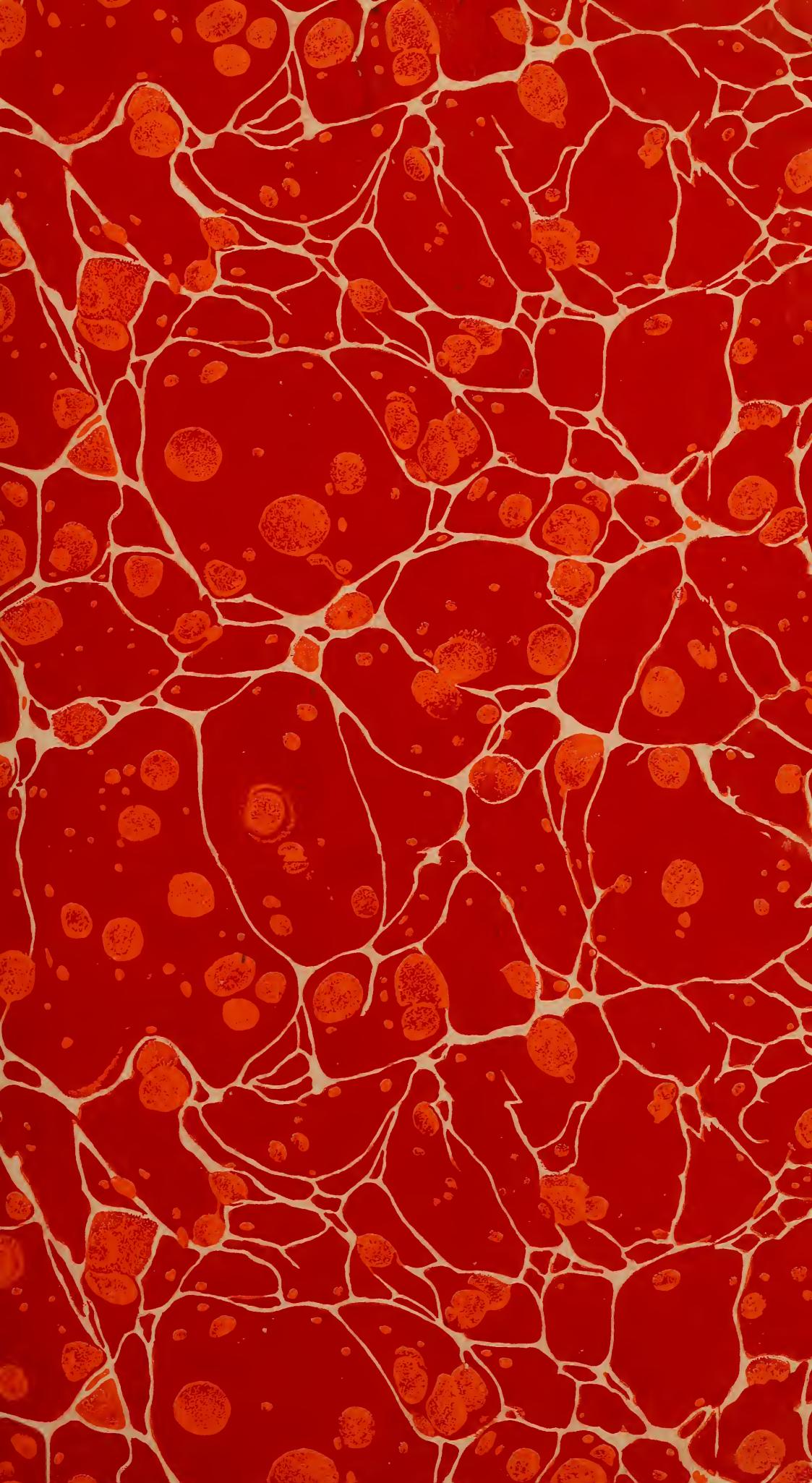


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THE PHOTOGRAPHIC EMULSION: AFTER-RIPENING

By Burt H. Carroll and Donald Hubbard

ABSTRACT

After-ripening is defined as the increase in sensitivity of photographic emulsions after washing. Following a discussion of the process, and review of the literature, the experimental methods of the National Bureau of Standards photographic emulsion laboratory are described in detail. After-ripening by digestion was studied with respect to eight of the more important variables. The amount of after-ripening which is practicable is dependent on the extent to which sensitivity nuclei have been formed during ripening before washing. The influence of temperatures and of bromide, chloride, and hydrogen ion concentrations, is according to predictions on the basis of chemical reactions forming sensitivity nuclei. The effect of gelatin-silver halide ratio can be explained by its influence on rate of development. Variations between different samples or makes of gelatin are illustrated. The progress of after-ripening with inert gelatin plus known sensitizing materials is very similar to that under the usual conditions, but there are important quantitative differences. The increase in practicable after-ripening with increasing percentage of silver iodide is illustrated. After-ripening during storage of finished plates was found to be similar to that by digestion, but frequently more efficient. Changes in bromide ion concentration during digestion, and in nonhalide silver during digestion or storage, are further proof of reaction during after-ripening, but it is evident that most of the nonhalide silver is photographically inert.

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I. INTRODUCTION

This paper is to be considered as a survey of its limited field rather than a completed investigation. Publication of the material here presented is dictated not only by the considerable length of the article but because the existence of this very important process is apparently

unknown to otherwise well-informed writers on photography. Recent literature has included specific if qualitative references (1), (2), (3), (4), (5)¹ to the fact that the sensitivity of an emulsion may be enormously increased by digestion *after washing*, but the general impression of the emulsion-making process is based on early literature (6) which cautions against such treatment.

We are unable to say how far our experiments correspond to commercial practice,² but some of the resulting emulsions are quite similar to very fast commercial products. We are also uncertain how much of the material presented may be common knowledge among emulsion makers, but it has never been published in quantitative form and it seems particularly unlikely that any information on this subject is to be expected from commercial sources.

The term "ripening" has been used to include any digestion or storage after mixing the emulsion, used to increase sensitivity. It is generally understood now, however, to mean digestion in the presence of excess soluble bromide, with or without the addition of ammonia. In the presence of these solvents for silver halide, there is a continuous increase in average size of the silver halide grains, with complicated changes in the size distribution. We will use "ripening" in this sense. "After-ripening" will be understood to mean changes in sensitivity after the silver halide solvents have been removed by washing; it is therefore associated with no appreciable change in grain size. After-ripening is normally carried on by digestion of the melted emulsion after washing; we shall use the term digestion to imply heat treatment of the washed emulsion, as distinct from the ripening by heat before washing. Marked after-ripening may also occur on storage of finished plates, especially if ripening and digestion have been limited; we shall refer to this as "storage ripening."

The impression which is given by the early literature is that the sensitivity of an emulsion is controlled almost entirely by the ripening and this is true of many of the older formulas.

Present procedure is apparently different; several authoritative statements to this effect have been published, for example, the following by Sheppard (Bogue, *Colloidal Behavior II*, p. 763):

These relatively coarse-grained negative emulsions are not produced from fine-grained emulsions by ripening, but the grain size is determined by the conditions of initial precipitation. High concentration of the reactants (AgNO_3 and KBr), low concentration of gelatin, high temperature of mixing, and retarded addition permit the process of recrystallization to take place at once, with the formation of definite, coarse-grained suspensions.

Our own experience is in excellent agreement with this, but it may be amplified to advantage at one point. If the silver solution is added to the bromide, the first grains are formed in the presence of a high concentration of the latter. Now the solubility of silver bromide in a solution of potassium bromide increases very rapidly with increasing potassium bromide concentration³ and the rate of ripening (or at least the rate of change in grain size) obviously will increase with the solubility (7) so that there is very rapid ripening during the mixing. If the addition of the silver solution is retarded, using either a

¹ Numbers in parentheses here and elsewhere in the text refer to the bibliography at the end of the paper.

² Lüppo-Cramer (reference 1) states that, contrary to a common impression, he has found no significant difference between large and small batches of emulsion made by the same formula, provided that all variables, such as the rate of mixing, were actually kept constant.

³ Approximately as the fifth power, Hellwig. Z. Anorg. Chem., 25, p. 183; 1900.

slow continuous stream, or "double emulsification" (8), (9), the ripening of the silver halide first formed may be carried to its practical limit by the time the mixing is completed, and little or no more ripening in the usual sense is desirable.⁴ Ripening is followed by washing the emulsion, removing the silver halide solvents, such as soluble bromide and ammonia, so that the grain size and distribution is fixed after washing. It is a common impression⁵ that sensitivity is also practically fixed. The emulsions described in the early literature were generally low in iodide and ripened for a long time with ammonia. Emulsions of this type can not be after-ripened to any considerable extent. With other formulas capable of producing emulsions resembling modern commercial products, the sensitivity just after washing may not be more than 5 per cent of the final value which is reached by digestion at temperatures of 35° to 65° C. Our experience is that it is impossible to make a satisfactory fast emulsion of the neutral ("boiled") type without after-ripening, and that it is at least very difficult to do without it in ammonia-ripened emulsions.

In case the emulsion is coated without digestion, there will, in general, be an increase in sensitivity, on keeping the plates, which equals or exceeds the increase which could be produced by digestion. This was frequently observed in the early days of dry plates; Eder (11) cited several conflicting observations on this point, and gave the weight of his opinion to the erroneous conclusion of Gaedicke that there was no increase in sensitivity on storage if no trace of ammonia remained in the emulsion. We have already commented briefly on this subject (7).

The number of variables in a photographic emulsion is such that a complete series of independent changes in each one is quite impracticable. We believe that we here present enough data to indicate the sign and order of magnitude of the effect which several of these variables have upon after-ripening, although the exact course of the process with a given formula must obviously always remain a matter for careful determination in each individual case.

The nature of the processes occurring during after-ripening will be discussed at more length in connection with the evidence offered in this paper. As already mentioned, the change in grain size is negligible, since the solubility of the silver halide is practically the same as in pure water. After-ripening is primarily the period of formation of sensitivity nuclei. Thiocarbamides and related sulphur compounds have formed insoluble molecular compounds (12) with the silver halide during the mixing and ripening, but in the absence of ammonia, there is little rearrangement of these to form silver sulphide until the bromide ion concentration has been reduced by washing. Reduction of silver bromide to metallic silver also leaves soluble bromides as a product of the reaction and, therefore, must be much more rapid after washing; to date, there is neither positive proof or dis-

⁴ We have already (7) mentioned the marked increase in speed and decrease in contrast produced by slow mixing of a neutral emulsion. Lüppo-Cramer (1) has recently given further illustrations of this, with characteristic curves. Conditions in an ammonia process emulsion are much more complicated because of the competing formation of two kinds of complex ions $(Ag(NH_3)_2)^+$ and $(AgBr_x)^-$, but the wider range in grain sensitivity is still observed, with similar changes in the characteristic curve. Wall (10) has also discussed some of the consequences if the method of mixing the emulsion is varied, for example by addition of the silver and bromide solutions simultaneously to the gelatin; but we doubt if the evidence supports his view that a "slow form" of silver bromide is formed in the presence of a high concentration of soluble bromide.

⁵ For example, Neblette, "Principles and Practice of Photography" p. 162, 1926, says that after washing "The emulsion may be regarded as complete."

proof that this reaction is a source of sensitivity nuclei, but the writers agree with Lüppo-Cramer that it is very probably an important part of after-ripening.

II. EXPERIMENTAL METHODS

1. SENSITOMETRY

The usual methods of this bureau were employed—nonintermittent time scale exposure at an intensity of 1 meter-candle, brush development in unbromided pyrogallol at 20° for 3, 6, and 12 minutes, and measurement of density in diffuse illumination by a Martens photometer, the density of the fog strip being automatically subtracted. The illumination was the quality of mean noon sunlight; the more recent tests were obtained with a lamp of color temperature 2,360° and the Davis-Gibson filter tentatively adopted at the International Congress; the previous source was a lamp operated at a color temperature of 2,810° K. and a Corning "Daylite" glass filter giving photographically equivalent quality. The emulsions were machine coated on 5 by 7 inch (or in a few cases 4½ by 6½ inch) plates; three test strips 1½ by 5 inches cut from the center of the plate and backed with black shellac. The coating was somewhat heavier than commercial practice; this minimizes the photographic effect of irregularities incident to coating small experimental batches, but it obviously increases the fog density. Because of the very rapid storage ripening in the undigested emulsions, the tests were always made soon after coating (in 12 to 40 hours after drying was complete, unless stated to the contrary). Excepting in Table 1, the term "speed" in all our tables refers to the National Bureau of Standards speed number, $10/i$. The inertia (i) is expressed in candle-meter-seconds. Subscripts, or subheadings under γ and fog, indicate the time of development in minutes; six minutes is approximately the normal time for this developer.⁶

Sensitometry of experimental emulsions unfortunately is especially subject to difficulties in assigning numerical values to the data, as almost invariably some members of a series of emulsions fail to have characteristic curves with satisfactory straight line sections. Our conclusions are in all cases based on comparison of the complete characteristic curves, but by giving both speed and γ in the tables, a reasonably adequate idea of the changes in effective sensitivity has been presented.

A complete set of data illustrating change of sensitivity during after-ripening is given in Table 1 and Figures 1, 2, and 3. We are indebted to Messrs. Raymond Davis and G. K. Neeland for exposures of emulsion 4-68 with sector wheels giving steps on the log E scale of 0.15 and 0.20, as our wheel is of the conventional H and D pattern (nine steps, each twice the preceding one). The characteristic curves for 6 and 12 minute development are plotted in Figures 1 and 2; Figure 3 and Table 1 give the numerical constants assigned to these curves, including speed numbers both by the B. S. system

⁶ The order of sensitivity of the experimental emulsions may be judged by comparison with commercial emulsions tested under the same conditions. A moderate speed negative emulsion, Eastman roll film, has a B. S. speed of 220, $\gamma = 0.88$; two very fast emulsions, the Hammer Press plate (emulsion 4063), and Eastman Hyper Press plate (emulsion 3082) have speed 660, $\gamma = 1.05$ for the former, and speed 1250, $\gamma = 0.86$ for the latter.

and by that proposed by Jones and Russell (13). In the latter system, the speed is taken as proportional to the reciprocal of the exposure (E_m) corresponding to the minimum useful gradient, which is taken as $G=0.20$. For purposes of comparison the maximum value of each of the curves in Figure 3 has been made equal to 1.00.

As in most of the other cases of after-ripening, the curves of 4-68 at various digestion times differ not only in speed but in contrast and shape. The variation in sensitivity can not be adequately expressed by any single constant, but the speed number based on minimum useful gradient is evidently the best approximation to such an expression. Speed numbers in both systems are found to be dependent on time of development, falling in line with the results

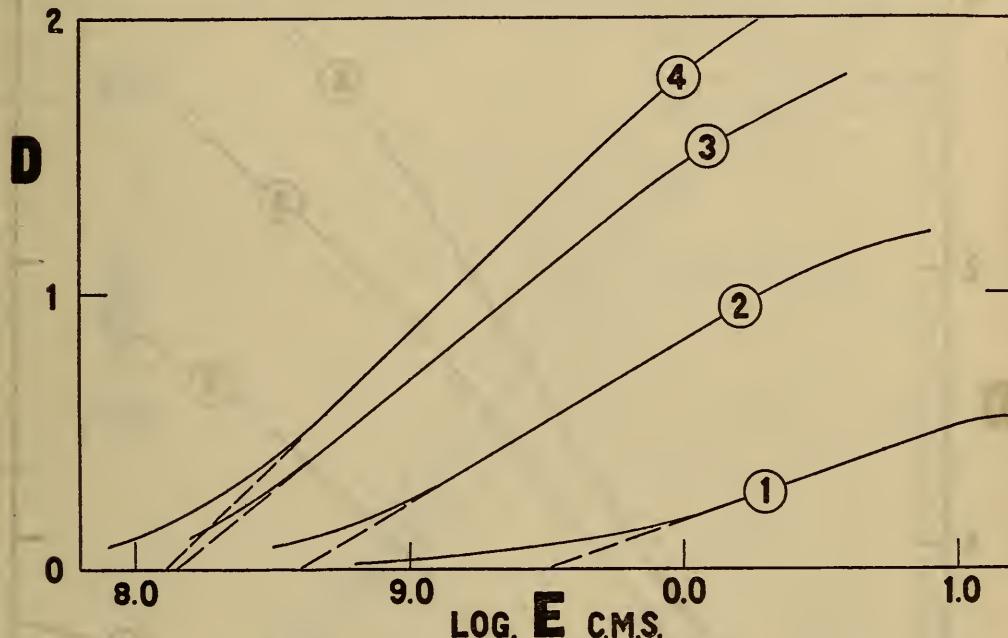


FIGURE 1.—Characteristic curves, 6-minute development of emulsion 4-68 at four stages of after-ripening

Digestion at 55° , pH 7 $[Br^-] 5 \times 10^{-3} N$. Curve 1, minimum digestion; curve 2, 1.0 hour; curve 3, 2.0 hours; curve 4, 3.0 hours

obtained by Davis and Neeland (14) with commercial emulsions. The reader is referred to their paper for a more complete intercomparison of the systems. The speed numbers given in this paper are an average value for the three times of development.

TABLE 1.—Comparison of methods of expressing sensitivity of emulsion 4-68 at different stages of after-ripening

Time of digestion (in minutes at 55°)	6-minute development				12-minute development			
	B. S. speed number $10/i$	γ	Jones and Rus- sell speed number $10/E_m$	Fog	B. S. speed number $10/i$	γ	Jones and Rus- sell speed number $10/E_m$	Fog
5	31.6	0.35	22.4	0.03	45	0.40	38.9	0.10
60	275	.57	455	.03	182	.92	435	.13
120	710	.81	1,200	.06	505	1.25	1,230	.18
180	735	.99	1,380	.09	435	1.71	1,445	.24

2. APPARATUS AND PROCEDURE USED IN EMULSION MAKING

The emulsions were mixed in batches using 30 to 60 g of silver nitrate (0.176 to 0.35 mol), the final volume being 0.7 to 1.5 liters. These were subdivided into batches of 0.044 mol (equivalent to 7.5 g AgNO₃) for comparison of differences in times of digestion or other variables. In all cases, the silver solution was added in a continuous stream to the mixture of bromide, iodide, and gelatin; the rate was varied over a considerable range by the use of separatory funnels fitted with capillary stems of different bores. The mixing vessel was a 1.5 liter Pyrex beaker, with a mechanical stirrer running 200 to

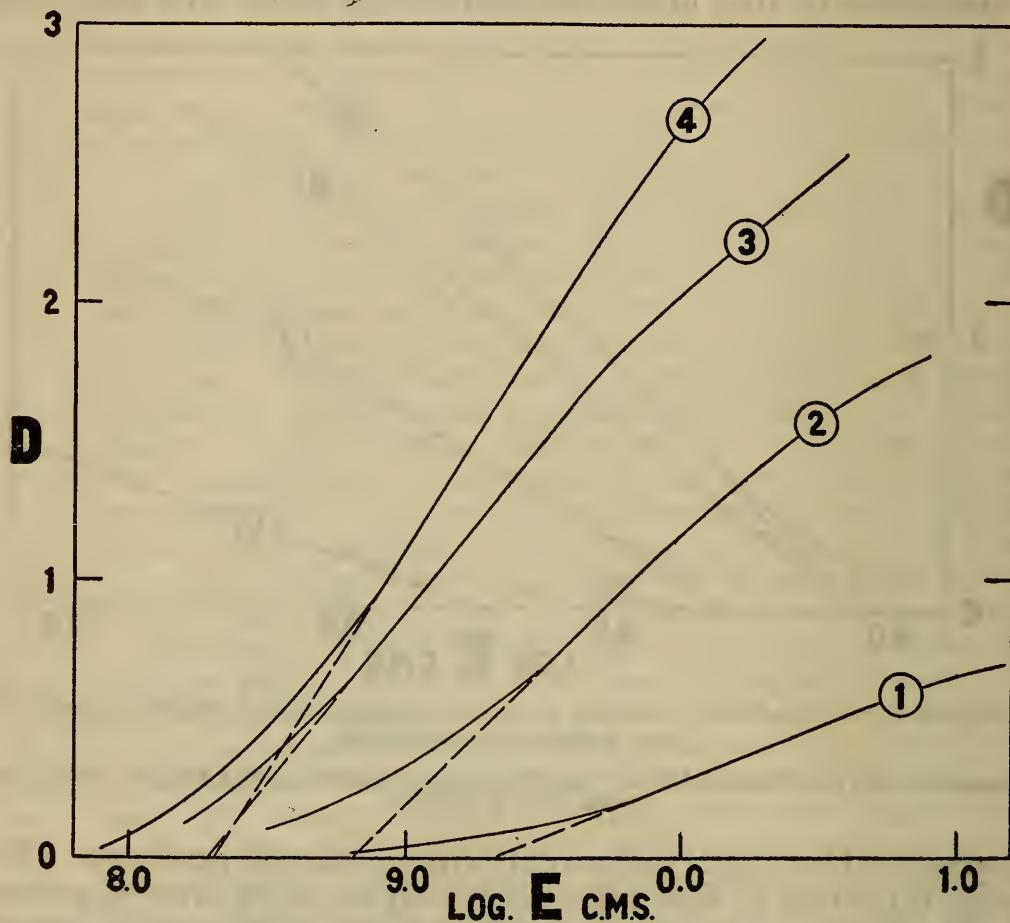


FIGURE 2.—Characteristic curves, 12-minute development, of same emulsion as in Figure 1

300 r. p. m. Using a silver shaft running in a glass bearing in the glass cover plate over the beaker, neither the liquid emulsion nor the condensate from it could come into contact with any material except glass or silver. Silver in contact with liquid emulsion was found to blacken quite rapidly in use, apparently from formation of silver sulphide (see Lüppo-Cramer (15)), so the actual stirrer was made of glass.

Both ordinary and centrifugal washing were used. For the ordinary method, the emulsions were rapidly chilled by pouring into a layer 1 to 2 cm thick in a clean enamelled tray floated on water at 5° to 8° C.; unless otherwise stated, they were left overnight at 5° to 8° C. before shredding and washing. Our shredding press forces the

set jelly through a sieve built up from sharpened metal strips set on edge, cutting it into clean "noodles" 5 to 6 mm square in cross section; there is very little formation of fine material, and consequently good circulation of water through the mass of "noodles." Using these relatively large but clean-cut noodles, we find that washing is more rapid than when the emulsion is, for example, shredded through netting into "noodles" which have more tendency to pack into a tight mass. The shredded emulsions were placed in silver-plated cans with 20-mesh screens of pure nickel at the bottom; these rested in slightly larger crocks, and the water, at the rate of at least 0.5 liter per minute, passed down through the emulsion and out over the edge of the crocks. Washington city water was used without treatment

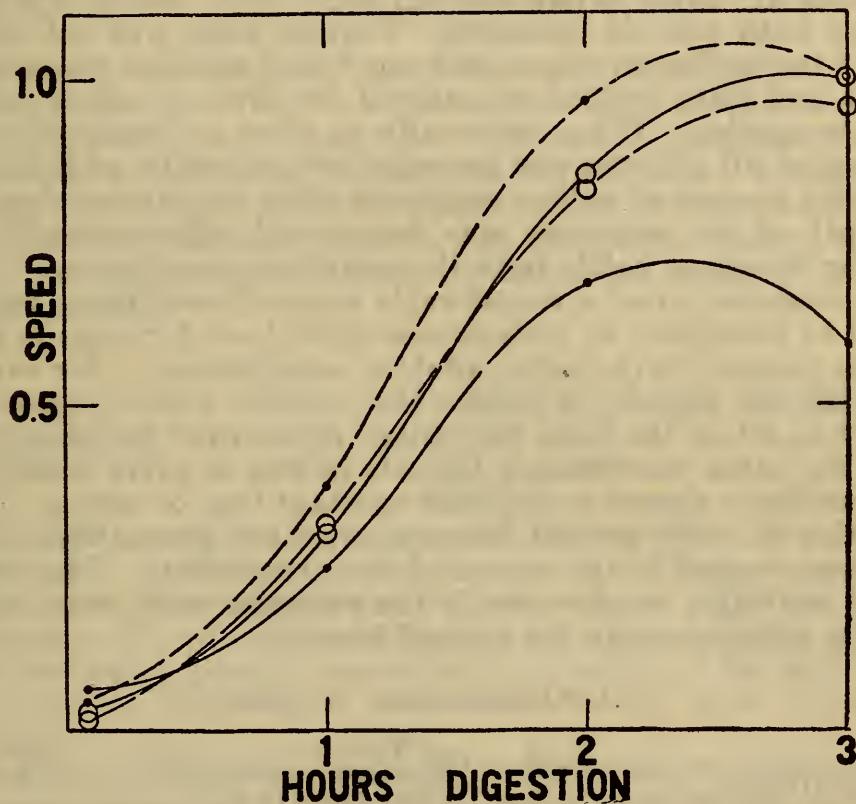


FIGURE 3.—Speed numbers of emulsion 4-68 at four stages of after-ripening by National Bureau of Standards (.) and Jones and Russell (o) systems, plotted against time of digestion

The maximum in each system has been made equal to 1. Dashed lines 6-minute development; solid lines, 12-minute development.

other than filtering and cooling; the normal temperature was 7° to 8° C., average hardness of the water, calculated as CaCO_3 , 80 mg per liter. The washing was very thorough, lasting 6 to 8 hours, with frequent hand stirring of the emulsion; for experimental purposes at least it is much more satisfactory to wash completely and add soluble bromides as desired, rather than to attempt to leave a definite amount. In the absence of ammonia in the emulsion, the pH after washing was 7 ± 0.5 ; if it was made with ammoniacal silver oxide, the pH might be as high as 8.5.

Our methods of centrifugal washing have already been described (7) (16); briefly, at the end of the desired ripening time, the silver halide is separated from the liquid emulsion, using a 5-inch imperforate

bowl at 3,000 r. p. m. The silver halide collects on the walls of the bowl in an adherent layer carrying considerable adsorbed gelatin, but is readily reemulsified by covering with 1.5 per cent gelatin solution and rubbing gently. This "wash suspension" is again centrifuged, and the silver halide suspended in the more concentrated gelatin (about 60 g per liter) used for coating; two separations reduce the bromide ion concentration to a value comparable with that after ordinary washing.

The emulsion was always stirred continuously during mixing and ripening. This was not always practicable during digestion, but stirring was in every case frequent enough to prevent appreciable sedimentation. All emulsions were filtered through very open (Whatman 41) paper before coating, and a little alcohol was added to break froth and aid spreading. Chrome alum was not used on many of the earlier emulsions, but was found essential whenever the Weigert and Lühr method of analysis for silver + silver sulphide was to be applied. It has apparently no effect on sensitivity except by changing pH (9); this was generally neutralized by addition of an equivalent amount of sodium carbonate after the chrome alum solution. pH of the emulsions was determined colorimetrically after removing the silver halide from the sample by centrifuging.

The emulsions cover a considerable range of conditions, but they may all be considered as variations of three basic formulas in which, as far as possible, only single variables were changed. For example, in varying the amount of iodide, the bromide was correspondingly changed to retain the same percentage excess over the silver; if the size of the batch was changed the rate of flow of silver solution was correspondingly altered to maintain constant time of mixing. In the description of each general formula, we have given those factors which were varied in the course of the experiments. The descriptions of individual batches specify the variables which were changed from the values given in the general formula.

A. "Full ammonia" formula

Water	ml	125	Water	ml	225
AgNO ₃ (0.176 mol)	g	30.0	NH ₄ Br (0.220 mol)	g	21.5
NH ₄ OH, concd. (0.353 mol) to redissolve			KI (0.00175 mol)	g	0.29
			Gelatin	g	12.5

The excess of soluble bromide was maintained at 25 per cent as given. The iodide as given corresponds to the formation of 1.0 mol per cent of AgI, assuming complete precipitation of the iodide, but iodide also was varied from 0 to 5 per cent. The solution of ammonia-silver oxide, at about 35°, was run into the halide-gelatin solution, held at 45.0° ± 0.5° in 2½ to 4 minutes; ripening was continued at 45° C.

In case centrifugal washing was used, nothing further was added to the emulsion before centrifuging. The quantity given was centrifuged in four batches; it was suspended again in 400 ml of 1.5 per cent gelatin, and might be stored over night at 5°, at this point. After centrifuging again, the emulsion was usually suspended in a total of 700 ml of water and 50 g gelatin; it was digested in this suspension. Where the effect of ripening time was under study, the four batches were taken out at intervals during ripening and kept separate thereafter. The necessary time for centrifuging four

batches was 20 to 25 minutes, so that there was always at least this much difference in the ripening time of the first and fourth.

For ordinary washing, 37.5 g of "secondary" gelatin, previously swelled for 20 minutes in cold distilled water, was added at the conclusion of ripening, and the emulsion rapidly chilled as soon as it was dissolved. It will be noted that the total amount of gelatin in the final suspension is the same in all cases, except in the emulsions where the gelatin-silver halide ratio was the variable under study.

B. "Full ammonia" formula

Water	ml	250	Water	ml	500
AgNO ₃ (0.353 mol)	g	60.0	NH ₄ Br (0.409 mol)	g	40.0
NH ₄ OH, concd. (0.71 mol) to redissolve			KI (0.0035 mol)	g	0.58

Gelatin

g 30.0

This formula was used only in one size batch, 60 g AgNO₃. Iodide was sufficient to give 1.0 to 5.0 mol per cent AgI, the excess bromide being kept constant at 17 per cent. The halide-gelatin solution was kept at 45.0° ± 0.5° during mixing, which took 4½ to 7 minutes, and ripening. After ripening to 25 minutes from the start of the mix, 70 g of swelled secondary gelatin was introduced, taking 7 to 10 minutes, and the emulsion chilled. Washing was always by the conventional method.

C. Neutral formula

Water	ml	450	Water	ml	350
AgNO ₃ (0.353 mol)	g	60.0	NH ₄ Br (0.429 mol) or equivalent		

KBr

KI (0.0139 mol)

Gelatin

g 42.0

g 2.30

g 20.0

The excess bromide is here given as 25 per cent, but 12.5 per cent was also used. Iodide was varied from 1 to 4.0 mol per cent. Time of mixing was also varied from 9 to 30 minutes. The usual temperature was 65°, but 55° and 52° were also used. Eighty grams of swelled secondary gelatin was added to a batch of the above size; unless otherwise specified, it was added directly after mixing was completed.

Centrifugal washing was used in a few cases; except in the specified cases, no secondary gelatin was added before centrifuging. The process was the same as in formula A.

3. ANALYTICAL METHODS

Bromide ion concentration in the emulsions was determined by the silver-silver bromide electrode at 30.0° C.: the apparatus is to be described in a future paper on some of the photographic effects of bromide ion concentration in the emulsion. It was not available for some of the earlier experiments.

The silver-silver bromide electrode is described in the literature as quite imperfectly reproducible, which is correct as compared to standard reference electrodes, but by using well-annealed silver wires, carefully cleaned whenever they showed signs of sluggishness, results were reproducible to ± 1 millivolt or better. This is fortunately negligible in determining any of the photographic effects of bromide ion concentration. Determinations in the emulsions are obviously favored by the enormous surface of the silver halide present, which maintains equilibrium.

III. EFFECT OF CERTAIN VARIABLES ON AFTER-RIPENING BY DIGESTION

1. RIPENING

Because of the limited capacity of our centrifuge, the data in Table 2 were necessarily obtained by making a series of emulsions, each subdivided into batches of different ripening time; digestion time was increased from the practicable minimum for all four batches of 8-101, to a maximum of 145 minutes for 8-99. The average grain

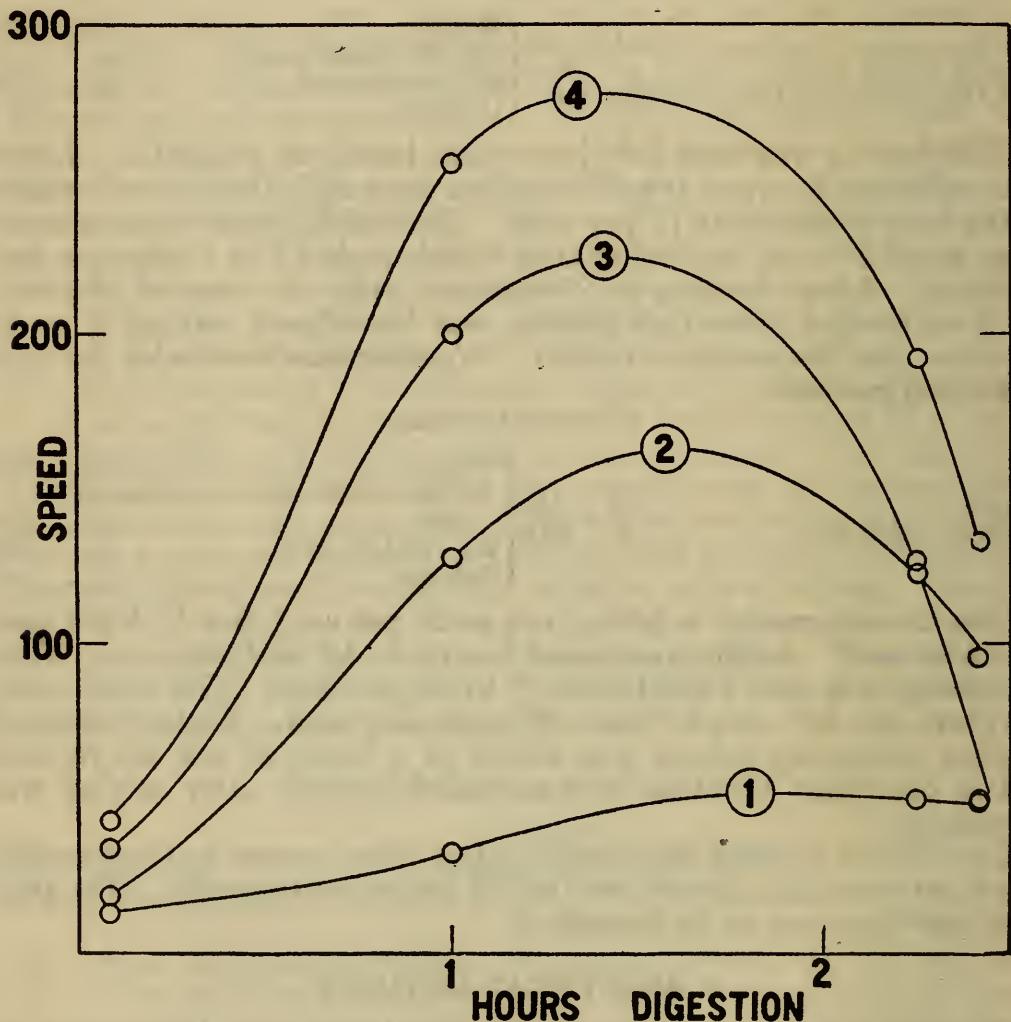


FIGURE 4.—Speed of centrifuged ammonia-process emulsions at four times each of ripening and digestion

Ripening time for emulsions in curve 1, approximately 5 minutes; curve 2, 0.5 hour; curve 3, 1.0 hour; curve 4, 2.0 hours

size increased normally with time of ripening: average projective areas for 8-100 were (1) $0.26 \mu^2$, (2) $0.39 \mu^2$, (3) $0.52 \mu^2$, (4) $1.00 \mu^2$. In view of the similarity of the other conditions, the differences in maximum speeds reached at optimum digestion times may reasonably be ascribed almost entirely to the change in grain size; a quantitative relation would be very difficult to obtain on these emulsions because of the heavy fog correction. In Figure 4, speed, for given ripening time, is plotted against digestion time; the data are seen to fall into a family of curves, with marked maxima. The optimum time of

digestion decreases as the time of ripening increases; as these emulsions were ripened in 0.9 N NH₃, there must have been relatively rapid formation of sensitivity nuclei during ripening, in spite of the presence of 0.11 N NH₄Br. The time of digestion to attain the optimum formation of nuclei is therefore reduced. It will be noted that the optimum digestion time is the same for one hour and two hours ripening and that the fog in the latter case is actually less; this has been previously observed. (See Table 1, reference 7.)

TABLE 2.—Effect of previous ripening on after-ripening during digestion

[Formula A, 1 per cent AgI centrifugal washing; Winterthur (8565) gelatin in mix digestion in untreated Winterthur (8565) gelatin]

Emulsion No.	Ripening time	Time of digestion	Speed	γ			Fog			
				3	6	12	3	6	12	
8-101-1	Minutes	Minutes at 45°		13	1.05	1.46	1.60	0.05	0.08	0.11
				<10	.50	1.15	1.40	.19	.26	.31
				<10	.34	.40	.67	.21	.32	.36
				<10	.34	.50	.60	.27	.52	.69
8-102-1	7	60	33	1.45	2.15	3.00	.10	.11	.15	
		33	128	.70	1.30	1.75	.22	.29	.39	
		63	200	.55	1.00	—	.27	.37	—	
		119	255	.45	.80	1.15	.27	.45	.57	
8-100-1	7	135	50	.95	1.45	2.03	.90	.13	.37	
		30	127	.70	1.05	1.55	.17	.26	.60	
		62	123	.70	1.03	1.37	.24	.46	.85	
		135	192	.57	.87	1.33	.28	.41	.82	
8-99-1	12	145	49	1.30	2.14	2.77	.06	.10	.25	
		35	96	1.04	1.53	1.95	.14	.27	.56	
		62	50	.70	1.20	1.47	.27	.56	1.01	
		120	133	.55	.87	1.23	.21	.49	.82	

TABLE 3.—Effect of previous ripening on after-ripening during digestion

[Neutral (C) emulsions; 1 per cent AgI; normal washing; Winterthur and Nelson No. 1 gelatin; digested at 45°]

Temper-ature of mix	Time of mix	Excess NH ₄ Br	Bromide ion con-centra-tion dur-ing diges-tion	Time of diges-tion	Speed	γ			Fog			Emul-sion No.	Aver-age grain size (pro-jective area in μ^2)	
						3	6	12	3	6	12			
65°	Minutes	Per cent	{ 1.6 \times 10 ⁻⁵ N}	Minutes at 45°	10	160	0.23	0.33	0.42	0.01	0.03	0.11	4-63-1	1.05
					60	245	.40	.63	1.01	.02	.05	.19	2	
					120	440	.46	.75	1.30	.06	.09	.25	3	
					180	505	.65	.80	1.45	.06	.11	.29	4	
55°	31½	25	{ 1.4 \times 10 ⁻⁵ N}		10	80	.25	.36	.48	.00	.02	.05	4-62-1	.53
					80	175	.63	1.09	1.56	.04	.06	.11	2	
					160	265	.81	1.25	1.83	.05	.07	.15	3	
					240	290	.80	1.35	1.89	.08	.11	.20	4	
52°	25½	12.5	{ 1.8 \times 10 ⁻⁵ N}		10	34	.36	.55	.66	.02	.04	.08	4-64-1	.34
					60	120	.84	1.22	1.75	.07	.10	.18	3	
					130	205	.92	1.14	1.88	.06	.17	.30	5	
					240	215	1.00	1.55	2.23	.16	.22	.39	7	

¹ Bromide ion concentration 7.6 \times 10⁻⁴N.

The data on neutral emulsions with the same percentage silver iodide, show the expected differences in maximum speed corresponding to changes in grain size.

The time required for digestion to maximum speed was about 220 minutes for emulsion 4-62, 195 minutes for 4-64, and 180 minutes for 4-63. It was thus reduced by increase in temperature of ripening, and by decrease in excess of soluble bromide; both of these changes obviously favor the formation of nuclei during ripening. In all three cases, it is considerably greater than is required for ammonia emulsions ripened to the same average grain size.

2. TEMPERATURE

The chemical reactions involved in after-ripening may be expected to have a temperature coefficient of two or more for every 10° . The correlation between these reactions and the photographic properties is unknown, but a similar temperature coefficient for after-ripening is a reasonable prediction. Tables 4, 5, 6, 10, and 11 show that it is verified under a variety of conditions. The rate of photographic change with time can not be satisfactorily expressed by any formula which we have tried, so we can obtain only a rough estimate. The time required to reach maximum sensitivity at 45° is about three times as great as at 55° ; taking the initial slope of the speed, time of digestion curve, the coefficient is about 4.

TABLE 4.—*Effect of digestion temperature on after-ripening*

[Neutral (C) emulsion 4-58; 4 per cent AgI; Winterthur and Nelson No. 1 gelatin; normal washing; $[Br^-] 2.5 \times 10^{-4}N$ at start of digestion; coating pH 7.2]

Digestion temperature	Time of digestion	Speed	γ			Fog		
			3	6	12	3	6	12
45.0°	Minutes							
	10	82	0.21	0.32	0.52	0.02	0.03	0.09
	60	137	.39	.67	.86	.02	.05	.14
	128	290	.47	.64	1.20	.05	.05	.11
	240	355	.62	.87	1.37	.06	.10	.17
54.2°	360	310	.58	.82	1.24	.21	.33	.51
	40	330	.60	.92	1.36	.03	.06	.17
	80	475	.56	.90	1.39	.09	.12	.18
	120	495	.55	.84	1.39	.10	.14	.22

TABLE 5.—*Effect of digestion temperature on after-ripening*

[Neutral (C) emulsion 4-65; 1 per cent AgI; Winterthur and Nelson No. 1 gelatin; normal washing; $[Br^-] 9 \times 10^{-4}N$, coating pH 7.0]

Digestion temperature	Time of digestion	Speed	γ			Fog		
			3	6	12	3	6	12
45°	Minutes							
	10	32	0.32	0.42	0.63	0.00	0.02	0.05
	75	55	.47	.70	1.16	.01	.02	.05
	135	81	.64	.81	1.43	.03	.05	.10
	240	140	.78	1.21	1.90	.05	.08	.14
55°	360	140	1.02	1.42	2.40	.22	.26	.45
	30	102	.52	.80	1.47	.02	.04	.13
	60	180	.73	1.20	2.03	.05	.07	.21
	90	195	1.02	1.44	2.10	.06	.08	.23

TABLE 6.—Effect of digestion temperature on after-ripening

"Full ammonia (B)" emulsion, No. 1-160; 5 per cent AgI; Nelson No. 1 gelatin; initial $[Br^-]$ during digestion $9 \times 10^{-6} N$, coating pH 6.9]

Digestion temperature	Time of digestion	Speed	γ			Fog		
			3	6	12	3	6	12
45°	10	81	0.30	0.33	0.37	0.00	0.03	0.09
	60	127	.84	1.16	1.60	.02	.06	.15
	120	230	.91	1.43	2.25	.04	.09	.19
	240	240	1.04	1.56	2.43	.06	.09	.21
	360	205	1.10	1.75	2.46	.08	.15	.27
54.5°	45	210	1.07	1.79	2.52	.05	.09	.19
	90	220	.91	1.42	2.37	.18	.27	.36
	135	143	1.10	1.75	2.45	.31	.48	.69

Neutral emulsions with 1 per cent AgI were digested at 45° and 55° in two narrow ranges of bromide ion concentration: Curves of speed against time are given in Figure 5 from data in Tables 5, 10, and 11. It will be noted that in the presence of added soluble bromide ($[Br^-]$ around $1 \times 10^{-3} N$), the temperature coefficient is greater than in the emulsion as washed ($[Br^-]$ around $1.8 \times 10^{-5} N$).

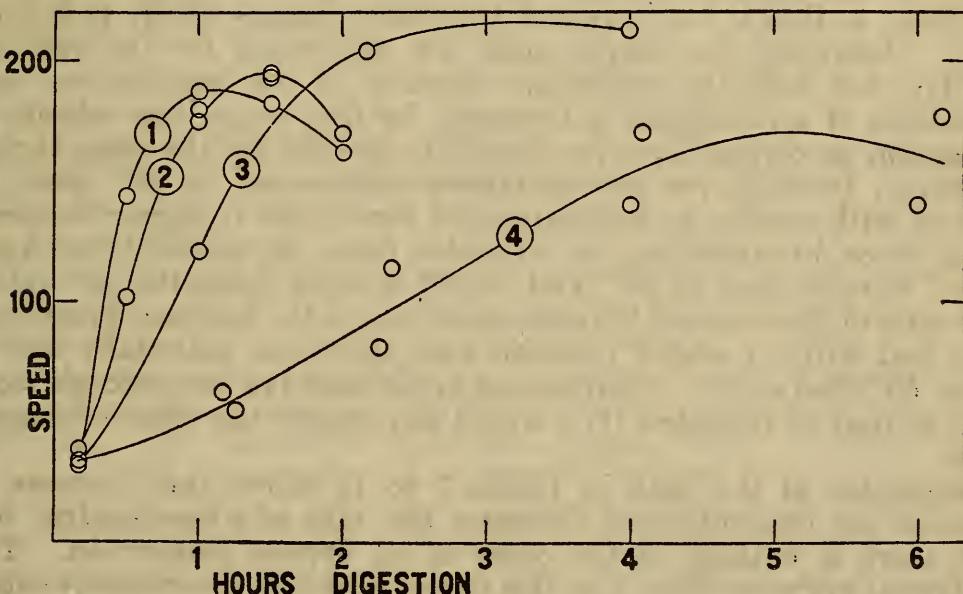


FIGURE 5.—After-ripening of neutral emulsions, 1 per cent AgI, under varying conditions of digestion

Curve 1, 55° , as washed; curve 2, 55° , with 5 KBr per 1,000 AgBr; curve 3, 45° , as washed; curve 4, 45° , with 5 KBr per 1,000 AgBr

The maximum sensitivity reached at 45° and at 55° C. is not widely different in any case. In spite of statements in the literature (3), (2), that low temperature and long time are generally desirable, 55° is very definitely better than 45° for the neutral emulsions with 4 per cent AgI. (Table 4.) In the neutral emulsions with 1 per cent AgI, the order depends on the bromide ion concentration during digestion. The ammonia process emulsion with 5 per cent AgI is slightly better at 45° . One feature of the long digestion at 45° is noteworthy—the sudden increase in fog after four hours (Tables 4, 5, and 10); this is not associated with sedimentation, since the emulsions were stirred continuously during this period.

3. BROMIDE ION CONCENTRATION

Any reaction forming silver or silver sulphide from silver bromide is practically sure to liberate bromide ions, the only other alternative being the formation of an un-ionized addition product. It is therefore obvious that after-ripening will be retarded by increasing bromide ion concentration,⁷ if it is actually a matter of the formation of silver or silver sulphide nuclei. The extent of the retardation may be expected to throw some light on the mechanism of the reaction, although interpretation of the photographic data is again handicapped because we do not know the relation between the extent of the reaction and the resulting changes in photographic sensitivity. Sheppard and his associates have shown that the formation of silver sulphide during after-ripening takes place by rearrangement of the adsorbed complex of silver bromide and sensitizer, and we believe that the evidence indicates that, if reduction to metallic silver plays a part in after-ripening, it takes place by a similar mechanism. It is at least quite improbable that sensitivity nuclei are produced by the reduction or other reaction of the silver halide in solution in the emulsion. It may safely be assumed that in the emulsion, with the enormous available surface of the silver bromide grains, the product of silver and bromide ion concentrations is practically constant⁸ at all times, so that if one is varied, the other changes nearly in inverse ratio. Assuming the simple mass law expression for the reaction of silver ion with the sensitizing material, if the bromide ion concentration of an emulsion is increased by fifty times, the velocity of a reaction involving silver ion should be divided by the same factor. However, bromide ion concentrations determined at 30° must be applied with caution to calculations of conditions at higher temperatures, since, interpolating the available data, the solubility of AgBr at 45° is twice that at 30°, and at 55° is three times the 30° value. The ratio of the bromide ion concentrations in the batches of emulsion with and without added bromide was, therefore, materially less at 45° or 55° than at 30°. Corrections to the mass law for ionic reactions such as that of Bronsted (17), would not change the order of magnitude.

Inspection of the data in Tables 7 to 14 shows that increase in bromide ion concentration decreases the rate of after-ripening, but that there is nothing of the order of an inverse proportion. The analytical evidence (Sec. V of this paper) which is theoretically much better than the photographic, is as decidedly against the hypothesis of an ionic reaction.

The curve of speed against time of digestion has a distinct S shape. This might be interpreted as an autocatalytic reaction; there is some justification for this, in that the formation of the new phase (Ag or Ag₂S) might catalyze the further breakdown of the silver bromide-sensitizer addition product. It is more likely that it represents the varying rate of change in photographic sensitivity with a relatively constant rate of reaction; if we assume that fog is caused by the formation of oversize sensitivity nuclei (18), the enormous increase

⁷ The concentrations used during ripening and digestion were of different orders of magnitude; the maximum amount present during digestion probably tends to decrease the solubility of silver bromide by mass action, rather than to raise it by complex ion formation as do the high concentrations used in ripening.

⁸ The solubility product of silver bromide is not affected by the gelatin (Winther, Trans. Faraday Soc., 19, p. 280; 1923); it must be slightly affected by the proportion of silver iodide, but our statement is correct for the results of adding soluble bromide to a given emulsion.

in fog, which can occur if after-ripening is continued too long, indicates that only a small proportion of the sensitizer has been used when the sensitivity reaches its maximum. On this basis, the relatively flat maximum found in most cases is readily explained by a balance between the grains still increasing in sensitivity and those lost by increase in fog or reduced in sensitivity by competition between nuclei (20). This reasoning must be used with caution, as the growth of fog has some of the characteristics of a secondary reaction. (See discussion (18).) This in turn may be explained by the very probable assumption that the hydrolysis of the gelatin during ripening or digestion continually liberates active sensitizing or fogging materials from less labile compounds. The curves of speed against time of digestion could not be fitted by any simple equation with sufficient accuracy so that the constants would be useful as a measure of change in sensitivity. One of the most obvious extensions of this investigation will be a more accurate and complete determination of the progress of after-ripening under known conditions, such as inert gelatin plus a sensitizer.

Tables 7 to 14 are designed to show the effect of bromide concentration during digestion, with a wide variety of emulsions. The most complete set of data on a single type are given in Table 9 and Figure 6. These represent the digestion of a high-speed type of emulsion as washed, and with three different additions of soluble bromide. On examination of Figure 6, the rate of after-ripening is seen to have decreased steadily as the bromide ion concentration was increased, but the speed for optimum digestion time rose to a maximum at $[Br^-] = 9.6 \times 10^{-4}$; the corresponding amount of bromide added, 5 KBr/1,000 AgBr, was of the same order as is found in most fast commercial emulsions (3 to 10 KBr/1,000 AgBr).⁹ The maximum speed fell off again when the bromide was increased to 20 KBr/1,000 AgBr ($[Br^-] = 4.7 \times 10^{-3}$), probably because the direct effect on sensitivity of a high bromide ion concentration (19) counteracts the favorable influence on after-ripening. Bromide present during digestion retards the increase in fog to a greater extent than the after-ripening. The increase in maximum speed which is permitted by the use of the proper amount of bromide appears to be greater than can be explained by the decrease in fog; the same problem comes up when increasing amounts of a nuclear sensitizer, such as allyl thiocarbamide, are added to emulsions under presumably constant digestion conditions (20). Sheppard has introduced the hypothesis of competition between nuclei on the same grain to explain the existence of an optimum concentration of sensitizer. This may equally well be applied to the existence of an optimum time of digestion, and less plausibly, to the increase in maximum speed obtained by adding bromide before digestion. In this last case the reduced rate of reaction might favor the continued growth of a single nucleus as against the further formation of new ones. Many of our emulsions (Sec. IV of this paper) have reached higher sensitivity by storage ripening than by digestion; here we have a slow process in which the formation of a new phase might be strongly inhibited, so that again the

⁹ Our analyses, which agree with those published by the Eastman laboratories at various times, show that soluble bromide is either added after washing, or else the washing is stopped short of completion. Wall, *Photographic Emulsions*, p. 154, refers to the addition of bromide as "an heirloom from the early days when a clean-working emulsion was practically an exception," but present quantities are, instead, considerably larger than those recommended by Eder.

growth of a nucleus already started would be favored against the beginning of a new one.

The after-ripening of all the types of emulsion is qualitatively very similar. We may make the rough generalization that a given amount of soluble bromide ($5 \text{ KBr}/1,000 \text{ AgBr}$) retards after-ripening most in those cases where it is the most rapid at a given temperature; the ammonia-process emulsions furnish the examples of this, prob-

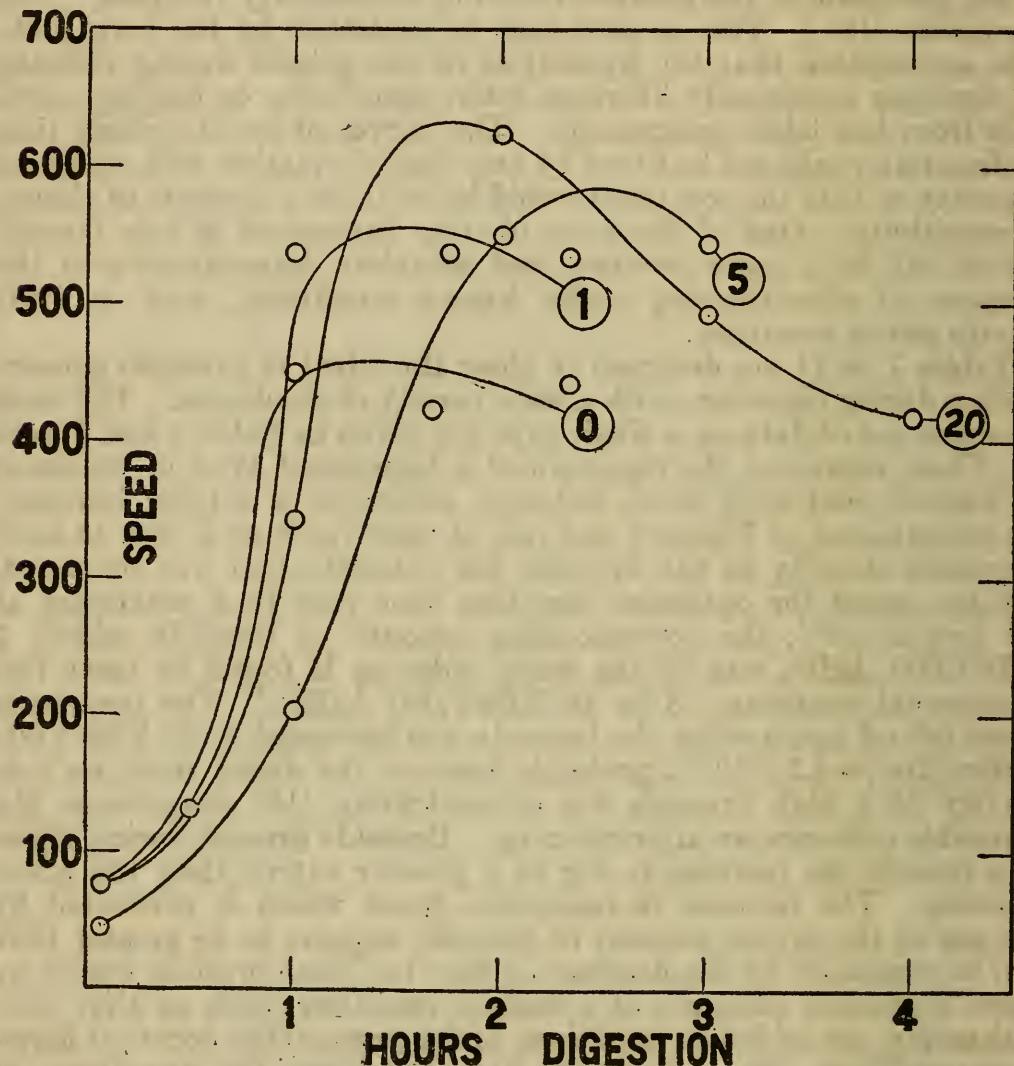


FIGURE 6.—After-ripening of neutral emulsions, 4 per cent AgI , at 55° , with varying concentrations of soluble bromide

Numbers of curves indicate the amount of bromide added, in terms of mols KBr per 1,000 mols AgBr

ably because of their higher pH. We have already observed the greater effect on emulsion 4-64 (Table 10) which was digested at 45° , as compared to the otherwise identical 4-66, digested at 55° (Table 11). Much more complete data will be necessary for mathematical analysis of any of the cases.

Increase in fog during after-ripening was less than we had expected. Table 12 gives an unusually favorable case in which there was actually a decrease. In general, the fog increases suddenly after a certain time, but this is usually past that required for the maximum sensi-

tivity: after-ripening is more likely to be limited by decrease in speed than by increase in fog. The addition of soluble bromide considerably increases the margin of safety in time between the points of maximum sensitivity and of rapid increase in fog, and reduces the rate of increase of fog during the useful period of digestion. We have already noted (p. 231) that the cases in which the sudden deterioration began before the maximum sensitivity was reached were on prolonged digestion at 45°.

TABLE 7.—Effect of bromide ion concentration during digestion on after-ripening [Emulsion 4-53; neutral "C" formula; 4 per cent AgI, 25 per cent excess NH₄Br; mixed at 65°; Winterthur gelatin; digested at 55°; coating pH 5.9]

Bromide ion concentration at beginning of digestion	Time of digestion	Speed	γ			Fog		
			3	6	12	3	6	12
$6.4 \times 10^{-6} N$ (as washed)	Minutes	42	0.31	0.48	0.63	0.02	0.05	0.09
		92	.58	.92	1.21	.02	.04	.13
		200	.63	1.01	1.25	.03	.07	.13
		350	.64	1.03	1.23	.05	.11	.17
$5.1 \times 10^{-4} N$ ($\frac{5 \text{ KBr}}{1,000 \text{ AgBr}}$)	Minutes	17	.27	.35	.40	.02	.04	.09
		31	.37	.57	.73	.02	.04	.09
		100	.43	.67	.96	.03	.06	.09
		270	.54	.86	1.08	.04	.07	.11

TABLE 8.—Effect of bromide ion concentration during digestion on after-ripening [Emulsion 4-59; 4 per cent AgI; 25 per cent excess NH₄Br; Winterthur gelatin; neutral mixed at 65° followed by ammonia ripening at 45°; coating pH 6.8. Digested at 55°]

Bromide ion concentration at beginning of digestion	Time of digestion	Speed	γ			Fog		
			3	6	12	3	6	12
$1.2 \times 10^{-5} N$ (as washed)	Minutes at 55°	70	0.34	0.50	0.66	0.03	0.04	0.13
		300	.63	1.07	1.49	.04	.10	.21
		390	.66	.94	1.24	.09	.11	.16
		340	.59	—	1.45	.20	—	.31
$3.3 \times 10^{-4} N$ ($\frac{2.5 \text{ KBr}}{1,000 \text{ AgBr}}$)	Minutes at 55°	182	.49	.85	1.15	.04	.08	.17
		400	.60	1.03	1.47	.06	.11	.24
		420	.53	.80	1.26	.15	.19	—
		315	.65	1.01	1.51	.19	.24	.34

¹ No decrease in effective sensitivity.

TABLE 9.—Effect, on after-ripening, of bromide ion concentration during digestion
[Emulsions 4-61 and 4-68; neutral (C), 4 per cent AgI, 25 per cent excess NH₄Br, Winterthur and Nelson No. 1 gelatin; mixed at 65° in 26-7 minutes]

Soluble bromide added after washing	Bromide ion concentration at beginning of digestion	Time of digestion	Speed	γ			Fog			Emulsion No.
				3	6	12	3	6	12	
<i>Minutes at 55°</i>										
None-----	$1.5 \times 10^{-5} N$ -----	60	450	0.81	1.04	1.50	0.09	0.14	0.26	4-61-2
		100	425	.65	1.06	1.60	.19	.34	.54	4
		140	440	.64	.96	1.50	.22	.43	.67	6
1 KBr 1,000 AgBr-----	$1.5 \times 10^{-4} N$ -----	30	132	.51	.83	1.24	.02	.04	.14	4-68-1
		60	535	.54	1.23	1.45	.06	.10	.20	2
		105	535	.57	.99	1.56	.10	.18	.29	3
		140	535	.66	1.06	1.65	.10	.18	.31	4
5 KBr 1,000 AgBr-----	$9.6 \times 10^{-4} N$ -----	5	76	.16	.20	.32	.03	.08	.13	4-61-1
		60	345	.46	.76	1.24	.05	.08	.14	3
		120	625	.64	.90	1.53	.08	.13	.18	5
		180	495	.66	.90	1.43	.16	.29	.37	7
		240	420	.66	1.12	1.68	.13	.24	.40	8
20 KBr 1,000 AgBr-----	$4.7 \times 10^{-3} N$ -----	5	45	.21	.25	.47	.00	.02	.05	4-68-5
		60	205	.35	.53	.80	.01	.03	.06	6
		120	550	.42	.73	1.20	.04	.05	.11	7
		180	545	.50	.90	1.54	.06	.09	.16	8

TABLE 10.—Effect of bromide ion concentration during digestion, on after-ripening
[Neutral (C) emulsion No. 4-64; 1 per cent AgI, Winterthur and Nelson No. 1 gelatin; digested at 45°]

Bromide ion concentration during digestion	Time of digestion	Speed	γ			Fog			
			3	6	12	3	6	12	
<i>Minutes at 45°</i>									
$7.6 \times 10^{-4} N \left(\frac{5 \text{ KBr}}{1,000 \text{ AgBr}} \right)$ -----	<i>Minutes at 45°</i>	10	34	0.36	0.55	0.66	0.02	0.04	0.08
		70	62	.46	.77	1.13	.02	.04	.09
		140	114	.64	.94	1.20	.04	.07	.13
		245	165	.66	1.04	1.76	.07	.09	.16
		370	175	.71	1.13	2.11	.27	.46	.67
1.8 × 10 ⁻⁵ N (as washed)-----		60	121	.84	1.22	1.75	.07	.10	.18
		130	205	.92	1.14	1.88	.06	.17	.30
		240	215	1.00	1.55	2.23	.16	.22	.39

TABLE 11.—Effect of bromide ion concentration during digestion, on after-ripening
[Emulsion 4-66, neutral (C) formula, 1 per cent AgI; Winterthur and Nelson No. 1 gelatin; digested at 55°]

Bromide ion concentration at beginning of digestion	Time of digestion	Speed	γ			Fog			
			3	6	12	3	6	12	
<i>Minutes at 55°</i>									
$1.5 \times 10^{-5} N$ (as washed)-----	<i>Minutes at 55°</i>	30	150	1.12	1.83	2.35	0.09	0.13	0.22
		60	190	1.23	1.55	2.38	.15	.24	.37
		90	180	1.01	1.41	2.12	.13	.20	.36
		120	160	.83	1.60	1.91	.11	.21	.48
		5	39	.26	.33	.48	.00	.00	.03
$1.2 \times 10^{-5} N \left(\frac{5 \text{ KBr}}{1,000 \text{ AgBr}} \right)$ -----		60	175	.65	1.18	1.85	.03	.08	.18
		90	195	.80	1.26	2.29	.08	.11	.26
		120	170	1.02	1.63	1.88	.10	.14	.34

TABLE 12.—Effect on after-ripening of bromide ion concentration during digestion
[Emulsion 1-159; "B" formula, 5 per cent AgI, Nelson No. 1 gelatin. Digested at 45°, pH 8.3; coating pH 6.1]

Bromide ion concentration at beginning of digestion	Time of digestion,	Speed	γ			Fog		
			3	6	12	3	6	12
<i>Minutes at 45°</i>								
$3.3 \times 10^{-4} N$ (No bromide added after washing)-----	<10	59	0.41	0.63	0.95	0.01	0.06	0.19
	53	110	.65	1.37	2.27	.01	.07	.28
	110	200	.79	1.37	2.04	.01	.07	.16
	180	200	.85	1.56	2.32	.02	.06	.15
$5.8 \times 10^{-4} N$ (5 KBr per 1,000 AgBr added after washing)-----	<10	22	.25	.37	.44	.07	.09	.21
	60	28	.40	.81	1.00	.01	.06	.19
	120	49	.54	.93	1.16	.02	.07	.12
	205	92	.66	1.15	1.60	.01	.06	.09

TABLE 13.—Effect on after-ripening of bromide ion concentration during digestion
[Emulsion 1-161; "B" formula, 5 per cent AgI, Winterthur gelatin. Digested at 45°, pH 8.0]

Bromide ion concentration at beginning of digestion	Time of digestion,	Speed	γ			Fog		
			3	6	12	3	6	12
<i>Minutes at 45°</i>								
$1.8 \times 10^{-4} N$ (No bromide added after washing)-----	60	165	0.66	1.28	1.95	0.02	0.08	0.21
	130	320	.73	1.34	1.94	.04	.12	.27
	185	360	.82	1.47	2.14	.07	.12	.29
	<10	66	.22	.51	.61	.00	.03	.14
$8.6 \times 10^{-4} N$ (5 KBr per 1,000 AgBr added after washing)-----	90	115	.55	.89	1.12	.01	.04	.15
	180	240	.63	1.03	1.60	.02	.04	.14
	270	340	.71	1.15	1.68	.03	.04	.18
	360	400	.74	1.29	1.77	.11	.13	.24

TABLE 14.—Effect on after-ripening of bromide ion concentration during digestion
[Emulsion 1-162; "B" formula, 1 per cent AgI, Winterthur gelatin. Digested at 45°, pH 8.3]

Bromide ion concentration at beginning of digestion	Time of digestion,	Speed	γ			Fog		
			3	6	12	3	6	12
<i>Minutes at 45°</i>								
$1.75 \times 10^{-4} N$ (No bromide added after washing)-----	60	87	0.95	1.70	2.13	0.01	0.07	0.19
	120	105	1.10	2.04	2.72	.04	.09	.27
	180	108	1.16	1.94	2.72	.06	.13	.33
	<10	46	.88	1.23	1.59	.00	.02	.10
$8.6 \times 10^{-4} N$ (5 KBr per 1,000 AgBr added after washing)-----	60	60	1.00	1.36	1.63	.01	.02	.10
	125	75	.95	1.44	1.78	.00	.02	.09
	210	88	1.01	1.51	2.02	.01	.04	.16
	300	107	1.02	1.65	2.23	.00	.06	.19

4. COMPARISON OF BROMIDE AND CHLORIDE IONS

The effect of bromide and chloride ions on after-ripening would be expected to be qualitatively similar; a considerable quantitative difference is introduced because the solubility of silver chloride (in mols per liter) is sixteen times that of the bromide, and the effect of chloride on silver ion concentration is correspondingly smaller. We should hardly have taken up this point if commercial emulsions had not been found (by electrometric titration of extracts) to contain as much as 38 mols of soluble chloride per 1,000 of silver halide. This

amount can be introduced into the emulsion by adding gelatin after washing, since some brands, especially those of European manufacture, were found to contain as much as 3.0×10^{-4} mol of soluble halide per gram of gelatin. We have never found it necessary to use this procedure, but it is recommended in many emulsion formulas; the reason, when any is given, is to make the emulsion set more readily.

TABLE 15.—Comparison of effects of bromide and chloride ions on after-ripening during digestion.

[Neutral ("C") emulsions, Winterthur gelatin, normal washing]

Mol per cent AgI in emulsion	Soluble halide added after washing, in mols per 1,000 mols AgBr	Time of digestion, hours at 45°	Speed	γ			Fog		
				3	6	12	3	6	12
0.0	0	<0.2	44	0.47	0.78	0.87	0.09	0.18	0.28
	0	2.5	64	.58	.83	1.03	.10	.15	.28
	1 KBr	2.5	69	.70	1.12	1.30	.08	.23	.39
	50 NaCl	2.5	68	.50	.77	.90	.10	.20	.36
0.0	0	<.2	40	.48	.80	1.07	.08	.17	.33
	0	2.5	56	.68	1.00	1.21	.10	.19	.40
	1 KBr	2.5	61	.63	1.10	1.42	.08	.18	.36
	50 NaCl	2.5	39	.64	.93	1.14	.09	.18	.40
1.0	0	<.2	49	.46	.69	.92	.03	.04	.14
	0	2.5	82	.69	1.10	1.58	.05	.12	.25
	1 KBr	2.5	69	.67	.96	1.34	.02	.08	.18
	50 NaCl	2.5	84	.60	.86	1.30	.04	.09	.27
2.25	0	2.5	55	.61	.88	1.25	.03	.11	.20
	1 KBr	2.5	34	.44	.59	.80	.02	.05	.14
	25 NaCl	2.5	47	.44	.64	.90	.03	.08	.21
	0	<.2	57	.37	.54	.65	.05	.12	.21
2.25	0	2.5	70	.53	.74	1.12	.08	.14	.27
	1 KBr	2.5	63	.47	.67	1.03	.08	.13	.27
	50 NaCl	2.5	70	.37	.56	.80	.07	.14	.27

TABLE 16.—Comparison of effects of bromide and chloride ions on after-ripening by digestion

[("A") emulsions, Winterthur gelatin, normal washing]

Ripening temperature	Mol per cent AgI in emulsion	Soluble halide added after washing, mols per 1,000 mols AgBr	Time of digestion, hours at 45°	Speed	γ			Fog		
					3	6	12	3	6	12
40°	0.0	0	2.5	119	1.43	2.02	2.70	0.05	0.08	0.17
		1 KBr	2.5	39	1.35	1.90	2.35	.02	.07	.08
		25 NaCl	2.5	86	1.40	1.90	2.50	.02	.06	.11
	1.0	0	<.2	63	1.45	2.04	2.57	.05	.07	.13
		0	2.5	134	1.80	2.58	3.20	.05	.13	.21
		1 KBr	2.5	87	1.46	2.10	2.70	.02	.07	.10
	2.25	25 NaCl	2.5	150	1.55	2.10	2.90	.03	.11	.16
		0	<.2	27	1.70	2.30	2.60	.02	.08	.19
		0	2.7	58	2.25	3.30	4.60	.05	.10	.29
	0.0	1 KBr	2.7	34	2.00	2.60	2.80	.02	.07	.17
		25 NaCl	2.7	63	1.70	2.42	3.04	.03	.09	.25
		0	<.2	63	1.06	1.60	2.38	.06	.10	.24
45°	1.0	0	2.5	125	1.30	1.93	2.40	.06	.12	.30
		1 KBr	2.5	92	1.27	1.83	2.63	.05	.12	.29
		50 NaCl	2.5	141	1.23	1.63	2.32	.04	.11	.27
	2.25	0	<.2	61	.95	1.35	1.85	.03	.09	.25
		0	2.5	146	1.21	1.84	2.70	.06	.09	.34
		1 KBr	2.5	124	1.10	1.65	2.30	.04	.09	.28
	2.25	50 NaCl	2.5	167	1.12	1.45	2.15	.03	.11	.30
		0	<.2	44	1.22	1.90	2.30	.05	.10	.18
		0	2.5	77	1.58	2.24	2.95	.05	.13	.27
	1 KBr	2.5	55	1.55	2.40	3.00	.04	.08	.24	
		50 NaCl	2.5	79	-----	1.90	2.64	-----	.10	.27

The experiments recorded in Tables 15 and 16 were made earlier than those in Tables 1, 2, and 3; the silver electrode apparatus was not yet in use, and the emulsions were all digested for $2\frac{1}{2}$ hours at 45° .⁹ This was near the optimum time for digestion, without added halide, of all the emulsions on which this point had been determined. It was possibly too much for the pure bromide emulsions, and very probably too little for those with 2.25 per cent AgI, so the results are considerably confused by the varying positions of this single time on the curve; they illustrate more than anything else, the danger of this procedure. The obvious difference between chloride and bromide is the depressing action of the former on the contrast. Higher densities were selectively depressed, with the result that the speed number was frequently highest in the batch digested with chloride.¹⁰ It is impossible from these data to give an accurate estimate of the amount of chloride necessary to produce an effect equivalent to one part of bromide, but the ratio must be of the order of 50 to 1.

5. HYDROGEN ION CONCENTRATION

The reversible effect of hydrogen ion concentration on sensitivity was discovered by Rawling and Glassett (4) in an investigation of after-ripening. Rawling also mentions (9) the existence of an irreversible effect. We have measured changes in sensitivity in connection with the equilibrium between hydrogen ion, silver ion, and gelatin (to be published later), but have done relatively little with the important relation between hydrogen ion concentration and the rate of after-ripening.

The data in Table 17 make it possible to compare the after-ripening, during a single time of digestion, in two portions of the same emulsion at different hydrogen ion concentrations. Since figures are given for unripened and ripened portions at each value of pH, it is possible to eliminate the direct effect of hydrogen ion concentration on sensitivity; the work of Rawling (9) has shown that the ratio of sensitivity at two values of pH is unaffected by sensitization with thiocarbamide, and may, therefore, be expected to be independent of the degree of after-ripening. Comparing the ratios of the digested and undigested portions of both 1-148 and 1-149, it is evident that there was much less after-ripening at the lower pH. In emulsion 1-148, the speed of the undigested portion of pH 6 was 0.89 times that of the undigested portion of pH 8; the corresponding ratio for the portions digested without bromide is 0.56. In emulsion 1-149 the corresponding ratios are 0.85 undigested and 0.65 digested. In both emulsions γ was nearly independent of pH, so that the sensitivity ratio may be measured by the speed alone.

⁹ Data on the undigested emulsions are given for comparison in most cases.

¹⁰ The data on pure bromide emulsions, Table 15, show a higher speed for the batches digested with bromide than those digested as washed; this is almost certainly because the latter were past the optimum.

TABLE 17.—Variation in both hydrogen and bromide ion concentrations during digestion

[Emulsions made by "A" formula Winterthur gelatin]

Emulsion No.	Soluble bromide added after washing, mols per 1,000 mols AgBr	pH	Time of digestion	Speed	γ			Fog		
					3	6	12	3	6	12
<i>Hours at 45°</i>										
1-148, pure AgBr	0	8.1	<0.2	62	0.90	1.57	2.10	0.05	0.09	0.18
	0	8.1	2.3	126	1.12	1.74	2.26	.09	.13	.24
	2	8.1	2.3	70	1.00	1.70	2.10	.05	.09	.14
	0	6.0	<.2	55	.95	1.37	1.98	.06	.09	.21
	0	6.0	2.3	65	1.06	1.67	2.24	.05	.15	.25
	2	6.0	2.3	54	.88	1.50	2.02	.06	.09	.17
1-149 2.25 mol per cent AgI	0	8.2	<.2	33	1.55	1.80	2.40	.06	.12	.33
	0	8.2	2.5	45	2.15	3.05	4.40	.07	.14	.49
	2	8.2	2.5	37	1.86	2.60	3.70	.05	.14	.40
	0	6.5	<.2	28	1.67	2.26	3.00	.05	.12	.37
	0	6.5	2.5	29	1.90	2.78	4.28	.05	.17	.55
	2	6.5	2.5	13	1.90	2.64	3.90	.05	.14	.49

The emulsions listed in Table 18 were not tested without digestion, so that the reversible pH effect can not be eliminated; the object of this series was to compare the effect of a given addition of soluble bromide at two hydrogen ion concentrations. The result of changing pH before digestion is seen to be highly dependent on the gelatin, as already observed by Rawling for the reversible effect. The decrease in sensitivity with decreasing pH was greatest in emulsion 4-41. Emulsions 1-151 and 4-43, made with the same gelatin by different formulas, showed about the same effect, in agreement with the observations of Rawling; the magnitude is less than in 4-41. In emulsion 4-42, the normal effect of pH showed only on addition of bromide; when the emulsion was digested as washed, the very heavy fog at the higher pH indicates excessive after-ripening with consequent loss of speed, which obscures the normal effect. In this connection, it may be pointed out that, while our data agree with those of Rawling that the fog is practically independent of changes in pH just before coating, it is frequently dependent on pH during digestion.

In Tables 17 and 18 there are six cases in which a given amount of soluble bromide was added to two portions of the same emulsion, adjusted to different hydrogen ion concentrations. With the exception of emulsion 1-148, the bromide retarded after-ripening to a greater extent at the lower pH. The comparison was made only at a single time of digestion, and is less satisfactory than the complete curve of after-ripening against time, but it seems sufficient. This result may be stated in another way, that the effect of hydrogen ion concentration on after-ripening is greater at a lower bromide ion concentration. In this form, it may be predicted from the data on bromide ion concentration given in Table 18. On increasing the hydrogen ion concentration of an emulsion, there is a decrease in bromide ion concentration, because silver ions previously in combination with the gelatin are released. This decrease in bromide ion concentration acts in opposition to the increase in hydrogen ion concentration, since it accelerates after-

ripening. In thoroughly washed emulsions, with very low bromide ion concentrations, the proportional change in concentration is much larger than in those to which soluble bromide has been added after washing; the observed effect of changing pH is therefore less.

TABLE 18.—Variation in both hydrogen and bromide ion concentrations during digestion

[All batches digested two and one-half hours at 45°. Emulsion 1-151 made by formula "A"; emulsions 4-41, 42, 43 made by that given by Rawling, reference 9, with increased time and temperature for the addition of the neutral silver nitrate solution]

Emul-sion No.	Mol per cent AgI	Gelatin	Soluble bromide added after washing, mols per 1,000 mols AgBr	pH	Bromide ion concentration N	Speed	γ			Fog		
							3	6	12	3	6	12
1-151	1.0	UCOP 3029----	0.0	7.0	5.4×10^{-6}	97	1.16	1.77	2.54	0.04	0.08	0.25
			1.0	7.0	4.3×10^{-5}	75	1.08	1.50	2.20	.02	.07	.16
			0.0	5.7	1.0×10^{-6}	83	1.04	1.53	2.70	.01	.11	.22
			1.0	5.7	3.1×10^{-5}	58	.97	1.55	2.08	.00	.08	.21
4-41	4.0	Winterthur----	0.0	7.7	7.4×10^{-6}	405	.67	1.04	1.48	.28	.50	.74
			2.4	7.7	2.5×10^{-4}	360	.77	1.35	1.86	.08	.13	.24
			0.0	5.5	7×10^{-7}	135	.75	1.25	1.98	.10	.22	.37
			2.4	5.5	2.3×10^{-4}	88	.67	1.25	1.98	.02	.08	.18
4-42	4.0	UCOP R-1333-	0.0	7.8	8.5×10^{-6}	330	.71	1.07	1.50	.41	.76	1.37
			2.4	7.8	2.8×10^{-4}	290	.78	1.20	1.77	.24	.50	1.02
			0.0	5.9	1.1×10^{-6}	485	.63	1.15	1.80	.08	.24	.44
			2.4	5.9	2.4×10^{-4}	220	.83	1.40	2.10	.05	.20	.26
4-43	4.0	UCOP 3029----	0.0	7	8.5×10^{-6}	160	1.00	1.55	2.25	.07	.11	.21
			1.0	7.5	8.2×10^{-5}	130	1.03	1.52	2.18	.04	.08	.18
			0.0	5.7	1.3×10^{-6}	123	.91	1.51	2.40	.02	.09	.22
			1.0	5.7	5.6×10^{-5}	87	.96	1.52	2.44	.02	.08	.20

6. GELATIN

(a) GELATIN-SILVER HALIDE RATIO

The addition of gelatin to the emulsion after washing frequently results in a decrease in sensitivity. In a few cases only this can be explained by decreased after-ripening as the result of adding chloride with the gelatin. The effect of gelatin-silver halide ratio per se was determined by the use of the centrifuge process, portions of the silver halide from a single batch of emulsion being suspended and digested in varying amounts of gelatin. Table 19 gives the results with two concentrations each of three gelatins of varying activity, the entire experiment being repeated with a change in the gelatin used for emulsification. Table 20 gives data on a single emulsion, with four different concentrations of the same gelatin used for after-ripening. It is evident that the speed is practically unaffected, but there is an appreciable decrease in contrast with increasing gelatin concentration. In Table 20 the values of *c* and *u* for the underexposure region (22) show that the effect is essentially the same here. It may readily be explained by a decrease in the rate of development in the thicker film.

Tables 21 and 22 show the results of adding gelatin to washed emulsions at the start of after-ripening. The depression in contrast was produced in all cases. In the ammonia-process emulsions, the addition of untreated gelatin also produced a distinct decrease in speed, and usually an appreciable increase in fog. If the gelatin had

been thoroughly washed, or treated with ammonia and washed, before adding it to the emulsion, neither speed nor fog was affected and only the decrease in contrast was observed. The chloride in the untreated Winterthur gelatin amounted to 13 mols per 1,000 of silver bromide, which would be hardly appreciable. The pH of the ammonia-process emulsions was appreciably decreased, since the untreated Winterthur gelatin has a pH of 5.2, the Nelson No. 1, 7.0. This again is not sufficient to account for the results, although the sum of the chloride and pH effects would be appreciable. It is probable that in the ammonia-process emulsions, which were further sensitized (in the sense of formation of nuclei) before digestion, the addition of the untreated gelatin increased the amount of available sensitizers past the optimum.

TABLE 19.—*Effect of gelatin-silver halide ratio on sensitivity*

[“Full ammonia” (A) emulsions, 1 per cent AgI, washed by centrifuge and suspended in 3 different gels at 2 concentrations. All batches digested at two and one-half hours at 45°]

Gelatin used for mix and ripening	Gelatin used for digestion and coating	Gelatin-silver halide ratio	Speed	γ			Fog		
				3	6	12	3	6	12
Winterthur (8763) untreated emulsion 8-156.	Winterthur (8763) untreated	{ 1.51:1 2.31:1	{ 34 32	1.26 1.17	2.00 1.97	2.80 2.20	0.08 .07	0.17 .11	0.38 .25
	Winterthur (8763) washed	{ 1.51:1 2.31:1	{ 12.6 15.4	----- .84	1.41 1.26	1.78 1.46	.08 .06	.11 .14	.14 .20
	Drescher (6136) digested with NH ₃ and washed	{ 1.51:1 2.31:1	{ 14.9 13.8	1.50 1.05	1.82 1.54	2.30 1.85	.08 .08	.12 .13	.18 .19
	-----	-----	-----	-----	-----	-----	-----	-----	-----
Winterthur (8763) washed emulsion 8-155.	Winterthur (8763) untreated	{ 1.51:1 2.31:1	{ 78 72	1.01 .81	1.53 1.31	2.10 1.80	.14 .08	.24 .27	.55 .55
	Winterthur (8763) washed	{ 1.51:1 2.31:1	{ 11.6 11.4	1.00 .95	1.33 1.23	1.45 1.55	.08 .05	.11 .14	.18 .21
	Drescher (6136) digested with NH ₃ and washed	{ 1.51:1 2.31:1	{ 15.0 13.9	1.20 1.02	1.63 1.42	2.00 1.75	.07 .06	.11 .14	.21 .22
	-----	-----	-----	-----	-----	-----	-----	-----	-----

TABLE 20.—*Effect of gelatin-silver halide ratio on sensitivity*

[Centrifuge-washed (A) emulsion, 1 per cent AgI, suspended in washed Winterthur gelatin at varying gelatin-silver halide ratios, and digested two and one-half hours at 45°]

Ratio gelatin: Silver halide	Speed	γ			Fog			c	u
		3	6	12	3	6	12		
1.07:1	9.5	1.27	1.65	2.10	0.11	0.14	0.20	0.02	0.38
1.51:1 (normal)	9.	1.10	1.36	1.68	.06	.10	.18	.01	.30
2.14:1	9.	1.04	1.40	1.60	.06	.12	.19	.03	.30
3.01:1	9.	.85	1.06	1.58	.06	.11	.18	.01	.28

TABLE 21.—Effect on after-ripening of gelatin added after washing

[Gelatin was added to portions of the emulsion on remelting after washing, raising the gelatin-silver halide ratio from the usual 1.51:1 to 2.31:1]

Emulsion	Time of digestion	Gelatin added after washing	Speed	γ			Fog			pH
				3	6	12	3	6	12	
<i>Hours at 45°</i>										
1-139, "A" formula 1 per cent AgI.	0.2	None-----	30	1.54	2.10	2.42	0.01	0.08	0.18	8.0
	2.5	do-----	66	1.98	2.80	3.60	.04	.10	.28	8.0
	2.5	Winterthur (8763) untreated.	50	1.36	2.05	2.75	.07	.16	.44	7.5
	2.5	Winterthur (8763) digested with NH ₃ and washed.	63	-----	2.27	3.00	-----	.13	.25	8.0
4-28, "C" formula 12 per cent excess KBr 2 1/4 g AgI.	2.5	None-----	58	1.07	1.43	2.05	.12	.18	.42	7.0
	2.5	Winterthur (8763) washed in sheets.	61	.74	1.13	1.65	.08	.17	.34	7.0
	2.5	Winterthur (8763) washed in shreds.	69	.75	1.14	1.62	.08	.15	.34	7.0
	2.5	Winterthur (8763) digested with NH ₃ and washed.	67	.78	1.17	1.67	.08	.18	.40	7.0
1-140, "A" formula 5 per cent AgI.	.2	None-----	41	.53	.68	.77	.03	.12	.24	8.0
	2.5	do-----	140	1.27	1.76	2.05	.05	.12	.28	8.0
	2.5	Winterthur (8763) untreated.	102	1.06	1.60	2.34	.04	.14	.33	7.5
	2.5	Winterthur (8763) digested with NH ₃ and washed.	145	.87	1.27	1.60	.03	.14	.30	8.0

TABLE 22.—Effect on after-ripening of gelatin added after washing

Emulsion	Gelatin added after washing	Time of digestion	Speed	γ			Fog			
				3	6	12	3	6	12	
<i>Minutes at 45°</i>										
4-11, 5 per cent AgI 12 per cent excess NH ₄ Br Winterthur gelatin "C" formula.	None-----	10	20	1.00	1.30	1.70	0.05	0.08	0.13	
		75	92	1.15	1.85	2.07	.05	.14	.22	
		130	150	1.08	1.70	2.60	.04	.15	.37	
		195	155	1.07	1.65	2.50	.07	.17		
1-118, 1 per cent AgI Nelson No. 1 gelatin "B" formula.	60 per cent more-----	60	94	.86	1.37	1.57	.05	.12	.17	.38
		120	165	1.00	1.60	1.70	.04	.14	.26	
		180	205	.90	1.40	1.97	.05	.15	.39	
		10	62	.85	1.30	1.72	.06	.12	.27	
	None-----	75	195	.92	1.38	1.90	.06	.19	.42	
		135	255	.87	1.55	2.08	.09	.20	.56	
		210	240	.96	1.44	1.87	.10	.32	.70	
		60	75	.80	1.30	1.75	.09	.22	.50	
	60 per cent more-----	125	108	.71	1.10	1.61	.13	.35	.77	
		200	105	.63	1.10	1.50	.18	.41	.91	

(b) MAKE OR BATCH OF GELATIN

The results of the entire process of emulsion making are notoriously dependent on the gelatin which is used, and after-ripening is affected as much as any other step. We shall not attempt in this paper anything more than recognition of this fact, with a few illustrations of the results of substituting different gelatins in a given formula.

Table 23 compares results for the "C" formula, with 4.0 mol per cent AgI and 25-7 minutes mixing time. With suitable gelatin, such as the Winterthur-Nelson combination, this will give an emulsion which would be rated commercially as very fast. We have included results with a sample of deashed gelatin. The deashing

process can cause considerable deactivation, as first reported by C. R. Smith (21), but the connection between removal of ash and of sensitizing materials is apparently accidental; thorough washing with water alone will reduce the activity of most gelatins to a considerable extent. It will be noted that the maximum sensitivity in this case is reached in an hour, followed by relatively slow deterioration. The treatment of the gelatin used in emulsion 46-69, consisting of one-half hour digestion with normal ammonia at 45°, followed by washing for a day, is by no means a complete deactivation, but it approaches it about as nearly as any other which we have tried; it is particularly successful in reducing fog. It will be noted that the contrast of the emulsion is always low. The indications are that the more labile sensitizing materials have been removed, but that there is a reserve of less reactive substances which come into play only on long-continued ripening. Analysis by the method of Sheppard and Hudson (26) indicated that one-third to one-half of the labile sulphur had been removed. As this method uses digestion with concentrated ammoniacal AgCl as a test of lability, it includes sulphur compounds not labile under the conditions of emulsion making.

When two samples of gelatin are compared as to their value for photographic emulsions, the relative rating may be altered or even reversed by a change in the emulsion formula. This condition is to be expected on the very probable assumption that all gelatins contain a mixture of sensitizing materials of varying reactivity. The results of using a gelatin in a neutral formula with the pH never greater than 7 can not be expected to be the same as those from a "full ammonia" formula in which ripening is carried on at a pH of 11, with free ammonia present in a concentration of nearly half normal. Again, it is probable that the optimum ratio of silver or silver sulphide (as nuclei) to silver halide varies with the proportion of silver iodide, and with the conditions under which it is formed. With this in mind, it is not surprising that, for example, the relative behavior of Winterthur and Nelson No. 1 gelatins differs for all three classes of emulsions represented in Tables 23, 24, and 25.

The use of centrifugal washing, which we have found quite useful in some classes of experimental work, creates conditions during after-ripening which can not be made exactly the same as those after conventional washing. This may be illustrated by considering the case of a known sensitizer, allyl thiocarbamide. It is water soluble, and hence can be removed from gelatin by thorough washing. If present in a neutral emulsion during ripening, it forms the water-insoluble complex with silver bromide, which will go through either type of washing process practically unchanged, breaking down to silver sulphide during the after-ripening. If, therefore, untreated gelatin is used both for the original emulsification and for the final suspension of the silver halide, there will be present during after-ripening all the allyl thiocarbamide from both portions of gelatin. The use of washed gelatin for either mixing or digestion approaches, but hardly duplicates, the conditions of conventional washing. Table 26 shows the progress of after-ripening in emulsions of the "C" type, 4 per cent AgI with centrifugal washing; the mixing time was somewhat less than that of the emulsions in Table 23, giving less speed and more contrast. An active gelatin was used for the original mix (emulsification). In one case it was centrifuged without addition of the secondary

gelatin and suspended in untreated active gelatins; in the other the full quota of secondary gelatin was added, but the final suspension was in ammonia-treated gelatin. The maximum sensitivity was practically the same in both cases. After-ripening was more rapid in the first case. This is somewhat unexpected, as in the second case the silver halide might have carried with it sufficient sensitizer-silver halide complex without further contribution from the coating gelatin. Tables 27 and 28 illustrate the results of various combinations of active and deactivated gelatins used for mix and ripening, and for after-ripening and coating. In these ammonia emulsions, ripening in an active gelatin may produce the optimum effect, so that further use of active gelatin is a liability (emulsion 8-153); or else there may still be the normal difference between coating gelatins (emulsions 8-103 and 106). The ammonia treatment did not produce a uniform product, but the three treated gelatins are more nearly the same than in their untreated states.

TABLE 23.—Comparison of after-ripening in emulsions made with different gelatins
[Neutral emulsions, 4.0 mol per cent AgI; digested at 55° without addition of soluble bromide]

Gelatin	Time of digestion	Speed	γ			Fog			Emulsion No.
			3	6	12	3	6	12	
<i>Minutes at 55°</i>									
Winterthur (9262) ¹	2.5	17.3	0.27	0.35	0.40	0.02	0.04	0.09	4-53-1
	30	92	.58	.92	1.21	.02	.04	.13	4
	60	200	.63	1.01	1.25	.03	.07	.13	6
	100	350	.64	1.03	1.23	.05	.11	.17	7
Winterthur (9262) (60 per cent) and Nelson No. 1 (40 per cent) ³ ⁴	5	83	.21	.32	.52	.02	.03	.09	4-58-1
	40	330	.60	.92	1.36	.03	.06	.17	2
	80	475	.56	.90	1.39	.09	.12	.18	4
	120	495	.55	.84	1.39	.10	.14	.22	5
Deashed gelatin from limed calfskin stock, treated by Northrop and Kunitz method	2.5	8.9	.43	.54	.65	.00	.03	.12	4-67-1
	60	205	.76	1.43	2.22	.03	.10	.28	3
	120	160	.70	1.31	1.97	.16	.31	.46	5
	180	125	.81	1.27	1.83	.26	.51	.69	7
UCOP (3029) digested with NH ₃ and washed	15	95	.15	.26	.29	.02	.03	.11	4-69-1
	50	152	.16	.29	.34	.01	.01	.08	3
	90	150	.26	.44	.58	.01	.04	.08	5
	185	310	.50	.71	1.06	.07	.10	.20	7

¹ Coating pH 5.9.

² Figures for undigested portions are for those melted with addition of KBr.

³ Digested at 54°.

⁴ Coating pH 7.2.

TABLE 24.—Comparison of after-ripening in emulsions made with different gelatins
["Full ammonia" (B), 5.0 mol per cent AgI; digested at 45° without addition of soluble bromide]

Gelatin	Time of digestion	Speed	γ			Fog			Emulsion No.
			3	6	12	3	6	12	
<i>Minutes at 45°</i>									
Winterthur (9262)	5	66	0.22	0.51	0.61	0.00	0.03	0.14	1-161-1
	60	165	.66	1.28	1.95	.02	.08	.21	2
	130	320	.73	1.34	1.94	.04	.12	.27	4
	185	360	.82	1.47	2.14	.07	.12	.29	6
Nelson No. 1	10	82	.30	.33	.37	.00	.03	.09	1-160-1
	60	127	.84	1.16	1.60	.02	.06	.15	3
	120	230	.91	1.43	2.25	.04	.09	.19	5
	240	240	1.04	1.56	2.43	.06	.09	.21	7
	360	205	1.10	1.75	2.46	.08	.15	.27	8

TABLE 25.—Comparison of after-ripening in emulsions made with different gelatins
["Full ammonia" (B), 1 per cent AgI; digested at 45° without addition of soluble bromide]

Gelatin	Time of digestion	Speed	γ			Fog			Emul-sion No.
			3	6	12	3	6	12	
Winterthur (9262) -----	<i>Minutes at 45°</i>	46	0.88	1.23	1.59	0.00	0.02	0.10	11-162-1
		60	.95	1.70	2.13	.01	.07	.19	3
		120	1.10	2.04	2.72	.04	.09	.27	5
		180	1.16	1.94	2.72	.06	.13	.33	6
Nelson No. 1 -----	<i>Minutes at 45°</i>	62	.85	1.30	1.72	.06	.12	.27	1-118-1
		70	.92	1.38	1.90	.06	.19	.42	3
		130	.87	1.55	2.08	.09	.20	.56	5
		205	.96	1.44	1.87	.10	.32	.70	7

¹ [Br] $9.8 \times 10^{-4} N$; digestion of 3, 5, and 6 at [Br⁻] $1.8 \times 10^{-3} N$.

TABLE 26.—After-ripening of neutral emulsions with centrifugal washing
[4 per cent AgI; mixing time, 18½ minutes. Coating pH 6.6. Winterthur (9262) gelatin in original mix]

Secondary gelatin	Coating gelatin	pH during digestion	[Br ⁻] during digestion	Time of digestion	Speed	γ			Fog			
						3	6	12	3	6	12	
None -----	{ $\frac{3}{5}$ Winterthur (9262) $\frac{2}{5}$ Nelson No. 1. }	6.2	$1.7 \times 10^{-4} N$	<i>Hours at 55°</i>	0.5	115	0.56	0.83	1.38	0.03	0.26	0.39
					1.0	175	.67	1.19	1.63	.20	.27	.45
					1.5	122	.80	1.15	1.99	.23	.34	.57
					2.0	110	.78	1.23	1.87	.26	.37	.59
Equal parts Winterthur (9262) and Nelson No. 1. -----	{ NH ₃ -treated UCOP(3029) }	7.3	$1.0 \times 10^{-4} N$	<i>Hours at 55°</i>	0.5	80	.30	.53	.77	.19	.28	.40
					1.0	150	.45	.74	1.13	.20	.28	.40
					1.5	180	.58	1.00	1.48	.19	.31	.40
					2.0	165	.59	1.03	1.53	.30	.51	.70

TABLE 27.—Comparison of after-ripening in emulsions washed in centrifuge and suspended in different gelatins

[Formula "A," 1.0 mol per cent AgI, digested at 45°]

Gelatin used for digestion and coating	Time of digestion,	Speed	γ			Fog			Emul-sion No.
			3	6	12	3	6	12	
Winterthur (8565) untreated -----	<i>Minutes at 45°</i>	24	1.17	1.78	2.06	0.11	0.14	0.23	8-103-1
		60	.94	1.77	2.37	.13	.19	.27	2
		120	126	1.05	1.65	2.25	.14	.24	3
		180	109	1.04	1.62	2.30	.15	.27	4
Winterthur (8565), previously digested with ammonia and washed -----	<i>Minutes at 45°</i>	18	1.23	1.80	2.15	.15	.18	.22	8-106-1
		60	17	1.43	2.10	2.58	.13	.17	2
		120	22	1.50	2.25	2.70	.16	.18	3
		180	35	1.55	2.10	2.50	.15	.20	4

TABLE 28.—Comparison of after-ripening in untreated and ammonia-deactivated gelatins

[Emulsions made by "A" formula, 1.0 mol per cent AgI; washed by centrifuge and suspended for digestion and coating in different gelatins. All batches digested 2.5 hours at 45°]

Gelatin used for mix and ripening	Gelatin used for digestion and coating	Speed	γ			Fog		
			3	6	12	3	6	12
Winterthur (8763) untreated. Emulsion 8-153.	Winterthur (8763) untreated-----	50	1.10	1.89	2.57	0.06	0.15	0.35
	Winterthur (8763) digested with NH ₃ and washed.	55	1.08	2.70	3.30	.05	.10	.18
	Drescher (6136) digested with NH ₃ and washed.	55	1.55	2.50	3.30	.05	.10	.18
	American Glue Co. "A" digested with NH ₃ and washed.	34	1.90	2.75	3.10	.05	.09	.18
American Glue Co. "A" digested with NH ₃ and washed. Emulsion 8-154.	Winterthur (8763) untreated-----	31	1.71	2.90	3.41	.08	.14	.27
	Winterthur (8763) digested with NH ₃ and washed.	15	1.63	2.35	2.53	.05	.10	.18
	Drescher (6136) digested with NH ₃ and washed.	12.5	1.95	2.48	2.95	.07	.13	.18
	American Glue Co. "A" digested with NH ₃ and washed.	12.6	1.87	2.32	2.63	.07	.11	.21

7. KNOWN NUCLEAR SENSITIZERS

It seemed instructive to make the comparison between after-ripening in emulsions made with active gelatin, and those made with deactivated gelatin plus definite amounts of sensitizing materials known to function by formation of silver sulphide nuclei. As already mentioned, it has so far been impossible to secure a completely deactivated gelatin, but there were available materials of activity very low compared to that of proper amounts of sensitizers. It should, perhaps, be pointed out that our experiments are not considered to represent the optimum results which can be obtained with allyl thiocarbamide or sodium thiosulphate; no attempt was made to do more than approximate the results obtained with active gelatin.

Neutral emulsions with 4 per cent AgI, on which the most after-ripening data were already available, were chosen for the comparison. In order to secure as nearly as possible the same conditions as with the natural sensitizers in gelatin, allyl thiocarbamide was introduced into the emulsions by swelling the secondary gelatin with a solution of it. Sodium thiosulphate had to be introduced after washing; a dilute solution was poured over the "noodles" before remelting. The allyl thiocarbamide can be introduced before washing, since it forms an insoluble addition compound with silver bromide (12), even in the presence of soluble bromide. Sodium thiosulphate must undergo a metathesis with silver bromide, liberating soluble bromide, before there is formed the silver thiosulphate which breaks down to silver sulphide. If introduced into the unwashed emulsion at a high bromide ion concentration, thiosulphate will, therefore, be lost on washing; this was verified by experiment. The metathesis equilibrium is probably far over toward silver bromide, and therefore quite sensitive to bromide ion concentration. The decomposition of silver thiosulphate liberates no bromide, and should be relatively independent of this variable as compared to the decomposition of the silver bromide-thiocarbamide complex. Both decompositions liberate acid, and should be retarded by increasing hydrogen ion concentration. Sheppard has stated that the formation of silver sulphide from thiocarbamides occurs at a "sufficiently alkaline reaction." Silver thiosulphate might decompose more rapidly in alkaline solution, but

all thiosulphates are unstable in acid solution, so that there is probably no pH at which it is stable.

The emulsions listed in Table 29 were made with a commercial sample of gelatin which, as shown by the control, was gratifyingly inert if the emulsion was made without addition of ammonia or other alkali. The data on addition of allyl thiocarbamide to an emulsion made with this gelatin are given to illustrate the marked effect of pH on the sensitization; on digestion at pH 6.3 the after-ripening was practically the same as in the control. The thiocarbamide was still there, since bathing in ammonia hypersensitized the finished plates,

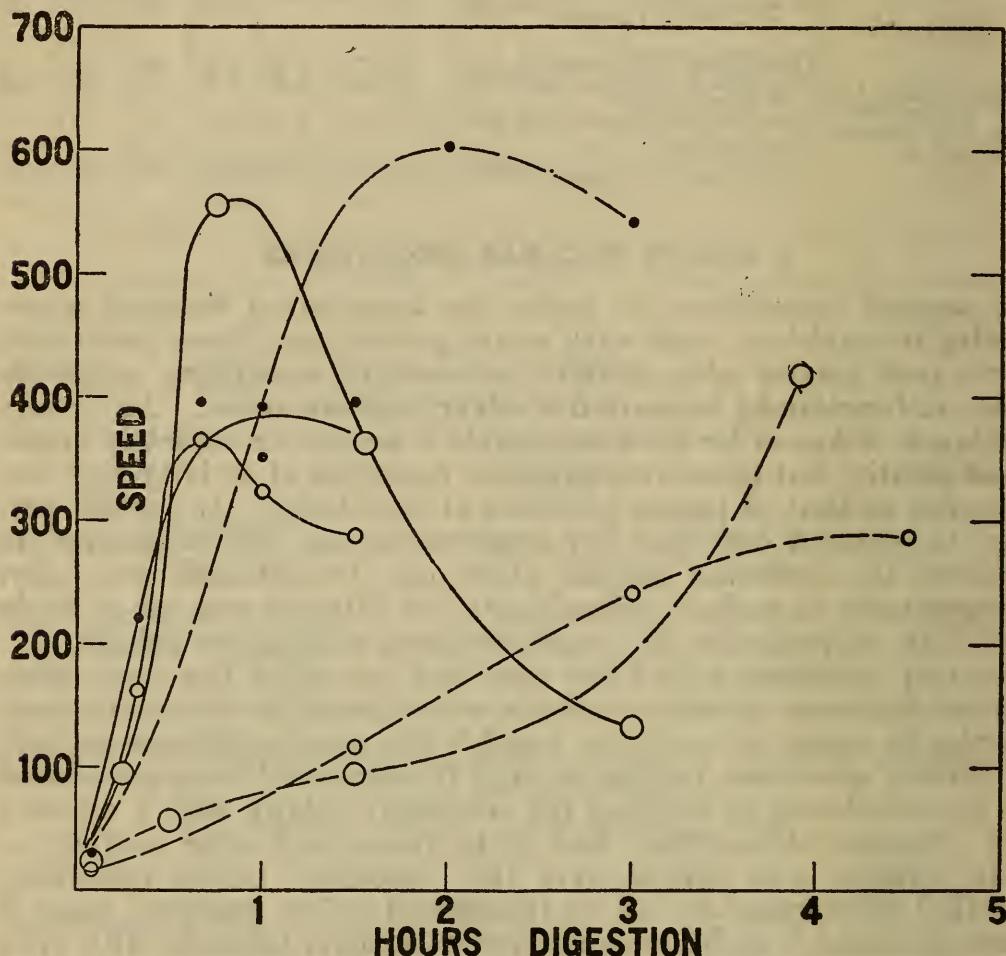


FIGURE 7.—After-ripening of neutral emulsions 4 per cent AgI, mixed with inert gelatin

Solid curves indicate digestion, at 55°, as washed; dashed lines, digestion at 55° with 5 KBr per 1,000 AgBr. ●, sensitized with active secondary gelatin; ○, O sensitized with allyl thiocarbamide sufficient to convert 1.6×10^{-8} and 2.4×10^{-8} , respectively, of silver bromide to silver sulphide.

but not those coated with the control emulsion. It is obvious that conditions of this nature may cause erroneous conclusions as to the value of sensitizing materials if the investigator has not given the attention to details which is necessary in photographic research. The emulsions listed in Tables 30 and 31 were made with different batches of ammonia-deactivated gelatin. At the higher values of pH in these emulsions, the gelatin was more active, especially on very long digestion.

After-ripening after addition of allyl thiocarbamide closely resembles that in active gelatin, as would be predicted from the natural occurrence of this sensitizer in gelatin. The qualitative similarity of the curves in Figure 7 is striking, and in view of the way in which

photographic sensitivity varies with small changes in conditions, the quantitative agreement is also good. It is strong proof that the processes occurring are of the same character in both cases. There is, however, an important difference which is evident on inspection of Tables 29, 30, and 31, and the curves. The presence of soluble bromide (5 KBr/1,000 AgBr) during digestion retards after-ripening with allyl thiocarbamide much more than with active gelatin. The difference is so marked that it seems a strong indication of the presence of other sensitizers in gelatin, although it can hardly be used as evidence of their character. The difference in the effect of bromide

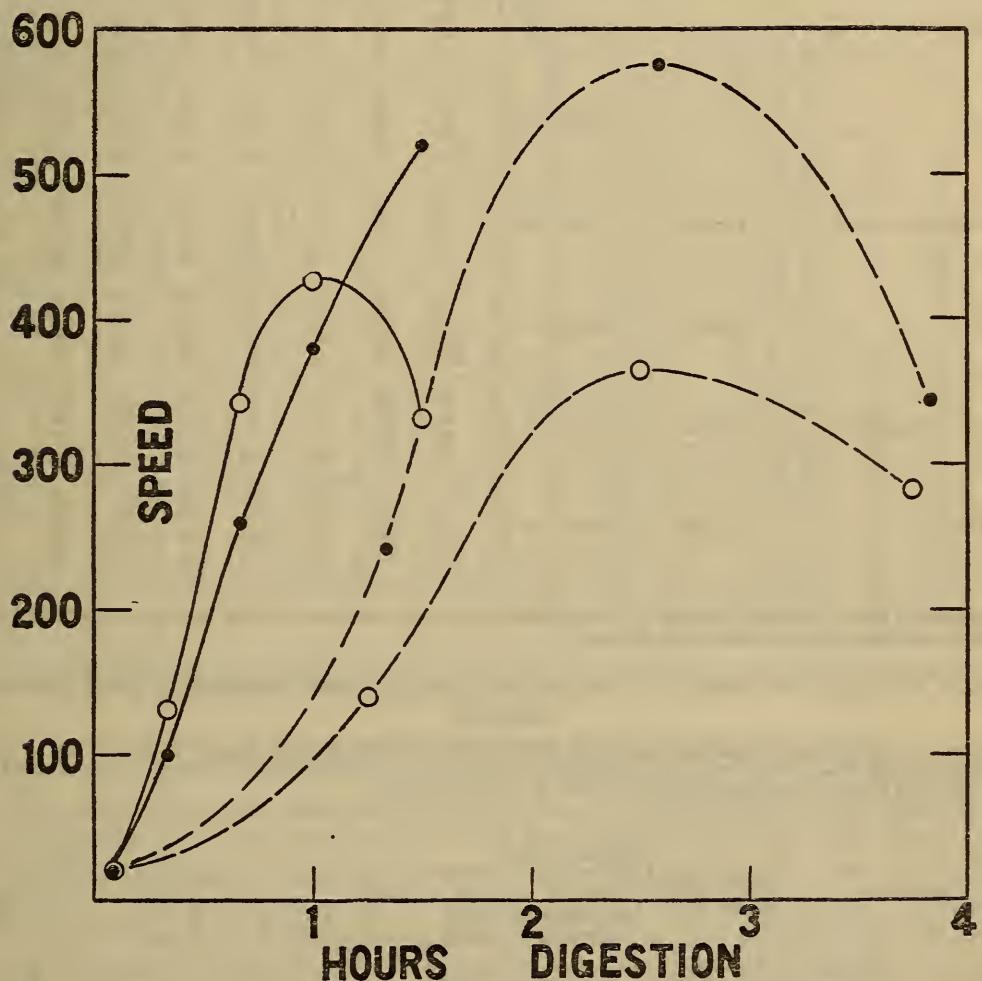


FIGURE 8.—After-ripening of neutral emulsions, 4 per cent AgI, made with inert gelatin and sensitized with sodium thiosulphate

Solid lines indicate digestion as washed; dashed lines, digestion with 5 KBr per 1,000 AgBr.
Digested at 55°; ●, pH 6.3; ○, pH 7.9.

appears in another way. With active gelatin, the maximum speed was higher at increased bromide ion concentration (figs. 3 and 5), but with either of the sensitizers the maximum was higher when the emulsion was digested without addition of bromide.

The data for sodium thiosulphate are presented in Tables 29 and 31 and Figure 8. They are very similar to those for active gelatin and allyl thiocarbamide. The decrease in rate of after-ripening produced by adding bromide is intermediate between the other two; it is greater at pH 7.9 than at pH 6.3. At pH 6.3, the after-ripening with thiosulphate has the peculiarity that the growth of fog is almost unaffected by the bromide.

TABLE 29.—*After-ripening in inert gelatin plus known amounts of sensitizers*

[Neutral (C) emulsions, 4.0 mol per cent AgI, made with commercial inert gelatin (UCOP 2939-1). The allyl thiocarbamide was added with the secondary gelatin; sodium thiosulphate was added after washing. pH during digestion, 6.3]

Sensitizer	$\frac{\text{Ag as } \text{Ag}_2\text{S}}{\text{Ag as } \text{AgBr}^1}$	Bromide ion concentration at beginning of digestion	Time of digestion	Speed	γ			Fog		
					3	6	12	3	6	12
None (control)	$1.1 \times 10^{-4} N$	<i>Minutes at 55°</i>	20 40 60 90	30 31 30 39	0.15	0.23	0.36	0.00	0.02	0.08
					.15	.25	.45	.02	.03	.09
					.19	.31	.50	.01	.03	.10
					.17	.31	.52	.00	.02	.09
Do	$7.9 \times 10^{-4} N$	<i>Minutes at 55°</i>	<5 90 180 270	15 29 46 78	.13	.16	.23	.00	.01	.04
					.17	.30	.40	.02	.02	.09
					.19	.36	.53	.00	.02	.11
					.23	.46	.70	.00	.05	.21
Allyl thiocarbamide	2.4×10^{-5}	$4.8 \times 10^{-5} N$	20 40 60 90	46 47 57 55	.14	.24	.37	.02	.02	.08
					.15	.27	.38	.01	.02	.08
					.17	.29	.41	.00	.02	.09
					.18	.33	.46	.00	.02	.09
Do	2.4×10^{-5}	$1.03 \times 10^{-3} N$	<5 90 180 270	25 61 83 99	.11	.14	.20	.00	.02	.04
					.13	.20	.30	.00	.02	.05
					.17	.30	.39	.01	.03	.08
					.21	.37	.48	.00	.03	.12
Sodium thiosulphate	2.3×10^{-5}	$2.9 \times 10^{-5} N$	20 40 60 90	100 260 365 520	.20	.42	.60	.02	.05	.11
					.38	.57	1.14	.02	.06	.24
					.38	.75	1.22	.02	.06	.25
					.46	.82	1.35	.02	.09	.34
Do	2.3×10^{-5}	$1.02 \times 10^{-3} N$	<5 80 155 230	19 240 575 345	.12	.13	.18	.01	.02	.08
					.22	.43	.72	.03	.08	.29
					.39	.61	.07	.04	.24	.73
					.41	.72	1.20	.06	.39	.96

¹ Assuming that the added sensitizer reacts completely with the silver halide, and not considering the unknown amount of Ag_2S from other sources.

TABLE 30.—*After-ripening in inert gelatin plus a known amount of allyl thiocarbamide*

[Neutral (C) emulsions 4.0 mol per cent AgI, made with ammonia-treated gelatin (UCOP 3029). Allyl thiocarbamide was added with the secondary gelatin of one emulsion; each emulsion was divided in halves, and digested with and without added KBr, at pH 7.5]

Sensitizer	$\frac{\text{Ag as } \text{Ag}_2\text{S}}{\text{Ag as } \text{AgBr}^1}$	Bromide ion concentration at beginning of digestion	Time of digestion	Speed	γ			Fog		
					3	6	12	3	6	12
None (control)	0	$2.2 \times 10^{-5} N$	<i>Minutes at 55°</i>	15 50 90 185	95	0.15	0.26	0.29	0.02	0.03
					152	.16	.29	.34	.01	.08
					150	.26	.44	.58	.01	.08
					310	.50	.71	1.06	.07	.26
Do	0	$1.4 \times 10^{-3} N$	<5 30 90 225	40 58 81 240	.12	.16	.20	.00	.02	.07
					.13	.18	.19	.00	.02	.07
					.17	.27	.34	.00	.03	.07
					.73	1.03	.04	.06	.06	.13
Allyl thiocarbamide	2.4×10^{-5}	$1.8 \times 10^{-5} N$	15 45 93 180	95 555 360 134	.33	.41	.61	.02	.03	.16
					.76	1.17	1.64	.03	.05	.23
					.69	1.35	1.95	.19	.34	.62
					.80	1.19	1.60	.55	.94	1.54
Do	2.4×10^{-5}	$1.15 \times 10^{-3} N$	<5 30 90 225	21.7 57 95 420	.20	.22	.26	.00	.02	.11
					.22	.23	.23	.00	.04	.12
					.25	.33	.37	.00	.03	.08
					.54	.86	1.34	.04	.07	.14

¹ Assuming that the added sensitizer reacts completely with the silver halide, and not considering the unknown amount of Ag_2S from other sources.

TABLE 31.—*After-ripening with allyl thiocarbamide, sodium thiosulphate, and naturally occurring sensitizers of gelatin*

[Neutral (C) emulsions, 4.0 mol per cent AgI, made with ammonia-treated gelatin (American Glue Co. "A"); secondary gelatin, the same where known sensitizers were used]

Sensitizer	Ag as Ag_2S Ag as AgBr	Bromide ion concentration at beginning of digestion	pH	Time of digestion <i>Minutes at 55°</i>	Speed	γ			Fog		
						3	6	12	3	6	12
Active secondary gelatin (Win- terthur and Nel- son).....	1.7×10^{-5}	6.8		20	220	0.54	1.07	1.16	0.11	0.15	0.21
				40	400	.67	1.13	1.57	.11	.17	.27
				60	350	.77	1.10	1.80	.19	.28	.36
				90	400	.70	1.33	1.93	.18	.27	.37
Do.....	8.6×10^{-4}	6.8		<5	36	.26	.34	.41	.00	.03	.08
				60	395	.61	.97	1.34	.06	.10	.14
				120	605	.64	1.06	1.63	.12	.18	.27
Allyl thiocarba- mide.....	1.6×10^{-5}	1.1×10^{-5}	7.9	20	162	.60	.93	1.95	.14	.20	.34
				40	365	.90	1.36	2.35	.13	.23	.41
				60	320	.87	1.36	2.30	.18	.31	.44
				90	290	1.08	1.53	2.10	.30	.50	.81
Do.....	1.6×10^{-5}	8.1×10^{-4}	7.9	<5	17	.41	.63	.79	.02	.06	.15
				90	117	.55	.70	.94	.02	.10	.16
				180	240	.57	.90	1.31	.05	.07	.21
				270	285	.74	1.13	1.62	.08	.13	.27
Sodium thiosul- phate.....	2.3×10^{-5}	1.0×10^{-5}	7.9	20	132	.72	1.06	1.69	.05	.10	.23
				40	345	.88	1.30	2.05	.09	.13	.29
				60	430	.87	1.26	1.98	.11	.18	.34
				90	330	.89	1.38	2.17	.19	.30	.44
Do.....	2.3×10^{-5}	9.2×10^{-4}	7.9	<5	24	.34	.36	.42	.03	.09	.17
				75	140	.74	.95	1.48	.04	.09	.20
				150	365	.87	1.28	1.98	.10	.16	.29
				225	285	.96	1.38	2.35	.15	.23	.41

¹ Assuming that the added sensitizer reacts completely with the silver halide, and not considering the unknown amount of Ag_2S from other sources.

8. PERCENTAGE OF IODIDE IN THE SILVER HALIDE

The use of a few per cent iodide in the silver halide is generally acknowledged to be necessary to a fast emulsion, but the literature gives little specific information as to the effects of variation in iodide content. It is impossible to decide from the available evidence whether there is a fundamental difference in the sensitivity of pure silver bromide and of mixed crystals of bromide and iodide. Huse and Meulendyke (23) have shown that as the percentage of iodide is increased the spectral absorption extends to longer wave lengths; it is very probable that the total energy absorbed from incident white light is also increased, but their data do not show whether the increase in absorption would cause an appreciable increase in sensitivity. Trivelli (24) suggested that the introduction of silver iodide into the silver bromide crystal lattice should cause a distortion of the latter; Wilsey (25), by X-ray crystal analysis, found that the spacing of the lattice was definitely increased, which might set up strains resulting in greater photochemical sensitivity. Our experiments are entirely too limited for generalization on this subject, but in the neutral emulsions compared in Table 32, we have an example of the type of data which we hope at some time to secure in sufficient quantity to be conclusive. By reducing the temperature of mixing and the excess

of ammonium bromide, the emulsions with 1 per cent silver iodide were made to have the same average grain size as those with 4 per cent; the distribution of grain size was similar, although not identical. Both were digested to optimum sensitivity under similar conditions, the time being shorter for the emulsion with less iodide. The difference in maximum speeds under these conditions appears to indicate an inherent difference in the sensitivity of the two mixtures of halides. The ammonia-process emulsions can not be compared at equal grain sizes, since the ripening was the same for both proportions of iodide,¹¹ but the evidence appears to be qualitatively the same.

Table 32 has been arranged to show the most definite connection between iodide content and after-ripening, which is that the practicable increase in sensitivity by after-ripening increases with increasing iodide. As would be expected, there is a considerable dependence on the gelatin and the emulsion formula. The emulsions with higher iodide content are notable for very low contrast before after-ripening; if the speeds before and after digestion were expressed by threshold value or by the system of Jones and Russell (13) instead of the H. & D. system, the ratio would be greatly increased.

Inspection of Tables 9, 11, 13, and 14 shows that the rate of after-ripening under comparable conditions decreases with increasing percentage iodide, but the difference is not large.

TABLE 32.—*Comparison of after-ripening in emulsions with 1.0 and 4.0 or 5.0 mol per cent silver iodide*

Formula and No.	Mol per cent AgI	Aver- age grain size	Gelatin	Digestion	Speed	γ			Fog		
						3	6	12	3	6	12
C, 4-68--	4.0	0.36^2	Winterthur-Nelson	{ Minimum--- Optimum---	76 625	0.16 .64	0.20 .90	0.32 1.53	0.03 .08	0.08 .13	0.13 .18
C, 4-65--	1.0	.34	do	{ Minimum--- Optimum---	39 195	.26 .80	.33 1.26	.48 2.29	.00 .08	.00 .11	.03 .26
B, 1-161--	5.0	.34	Winterthur	{ Minimum--- Optimum---	66 360	.22 .82	.51 1.47	.61 2.14	.00 .07	.03 .12	.14 .29
B, 1-162--	1.0	.37	do	{ Minimum--- Optimum---	46 108	.88 1.16	1.23 1.94	1.59 2.72	.00 .06	.02 .13	.10 .33
B, 1-160--	5.0	.33	Nelson	{ Minimum--- Optimum---	81 240	.30 1.04	.33 1.56	.37 2.43	.00 .06	.03 .09	.09 .21
B, 1-118--	1.0	.44	do	{ Minimum--- Optimum---	62 255	.85 .87	1.30 1.55	1.72 2.08	.06 .09	.12 .20	.27 .56

IV. STORAGE RIPENING

As already stated, after-ripening goes on slowly during storage of dried plates coated with undigested emulsions. Tables 33 to 38 give the data on storage ripening of several types of emulsions coated after varying amounts of ripening and digestion. To keep the tables from being too unwieldy, γ and fog are given only for 6-minute devel-

¹¹ It must be known to anyone with experience in emulsion making that, with the same ripening conditions, the grain size decreases with increasing proportion of iodide, but we have found only one explicit statement to this effect in the literature. Lüppo-Cramer (1) points out that pure bromide neutral emulsions have a grain very much larger than those with 1 per cent iodide, made under the same conditions. In addition to the data in Table 32, the grain size of emulsion 4-63, 1 per cent AgI, Table 3 may be compared with that of emulsion 4-68, 4 per cent AgI, Table 32 mixed at the same temperature with the same excess bromide.

opment; the speed number is also taken from that curve only instead of from the mean of the three. Random errors of coating and development are, therefore, more conspicuous than in the other tables. Considerably more data have been obtained than are given here.

Inspection of the tables shows that in every case the after-ripening on storage was at least equal to that on digestion; in general, it was somewhat greater. As would be expected, when the emulsion was digested to a maximum sensitivity, there was no after-ripening on storage; there was also the unexpected consequence that deterioration by fog in 1-year storage was generally less than in the undigested portions. Storage ripening in the neutral and ammonia-process emulsions was of the same order of magnitude, proving that it can not be ascribed to traces of free ammonia. (See p. 221 and reference 11.)

TABLE 33.—*Storage ripening of emulsion 4-11*

[“C” formula, 5.0 per cent AgI, 15 per cent excess KBr, Winterthur gelatin. All data for six minutes development]

	Time of digestion	Directly after coating			After 1 month storage			After 3 months, storage			After 12 months, storage		
		Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog
Digested as washed-----	Minutes at 45°												
	<10	20	1.30	0.08	105	1.45	0.09	220	1.60	0.11	125	2.05	0.47
	75	83	1.85	.14	110	1.65	.06	180	1.63	.12	160	1.93	.33
	130	160	1.70	.15	125	1.85	.09	140	1.85	.12	175	1.75	.32
Dry gelatin added after washing, 60 per cent of original amount-----	195	165	1.65	.17	165	1.80	.09	180	1.90	.13	180	1.90	.24
	60	87	1.37	.12	175	1.23	.09	230	1.35	.10	115	1.55	.31
	120	140	1.60	.14	190	1.42	.09	145	1.53	.12	130	1.58	.25
	180	195	1.40	.15	175	1.50	.11	110	1.68	.15	125	1.50	.24

TABLE 34.—*Storage ripening of emulsion 4-14*

[“C” formula, 1.0 per cent AgI, 16 per cent excess KBr, Winterthur gelatin. Digested as washed. All data are for six minutes development]

Time of digestion (minutes at 45°)	Directly after coating			After 1 month storage			After 3½ months, storage			After 13 months, storage		
	Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog
<10-----	45	1.00	0.05	180	1.45	0.07	315	1.77	0.17	210	1.78	0.55
65-----	63	1.50	.06	138	1.43	.09	230	1.58	.12	210	1.60	.34
125-----	100	1.78	.11	150	1.65	.08	210	1.77	.13	220	1.55	.30
180-----	125	1.80	.14	165	1.65	.09	220	1.87	.16	230	1.50	.29

TABLE 35.—*Storage ripening of emulsion 6-46*

[“C” formula, 5 per cent AgI, 16 per cent excess KBr, 14 minutes’ mixing time. Washed by centrifuge and suspended in untreated Winterthur gelatin. All data are for six minutes’ development]

Time of digestion (minutes at 45°)	Directly after coating			After 1 month storage			After 4 months’ storage			After 13 months’ storage		
	Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog
10±5-----	7.3	1.01	0.19	48	1.34	0.19	91	1.58	0.34	50	1.72	0.49
60±5-----	38	1.41	.23	69	1.42	.24	-----	-----	-----	60	1.83	.49
120±5-----	71	1.70	.27	87	1.60	.23	100	1.57	.35	72	1.75	.40
180±5-----	78	1.80	.30	87	1.75	.28	66	1.90	.35	66	1.77	.48

TABLE 36.—*Storage ripening of emulsion 6-48*

[“C” formula, 1 per cent AgI, 16 per cent excess KBr, 14 minutes’ mixing time. Washed by centrifuge and suspended in untreated Winterthur gelatin. All data are for six minutes’ development]

Time of digestion (minutes at 45°)	Directly after coating			After 1 month storage			After 3 months’ storage			After 12½ months’ storage		
	Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog
10±5-----	33	0.93	0.28	120	1.30	0.30	138	1.78	0.38	138	1.65	0.71
60-----	43	1.35	.28	105	1.32	.28	150	1.56	.37	160	1.72	.60
120-----	120	1.54	.29	115	1.60	.33	145	1.65	.40	145	1.58	.56
180-----	115	1.75	.36	132	1.74	.39	138	1.70	.49	132	1.65	.55

TABLE 37.—*Storage ripening of emulsion 1-118*

[“B” formula, 1 per cent AgI, Nelson No. 1 gelatin. All data are for 6 minutes development]

	Time of digestion	Directly after coating			After 25 days’ storage			After 3 months’ storage			After 13 months’ storage		
		Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog
Digested as washed-----	Minutes at 45° <10	62	1.30	0.12	160	1.18	0.10	260	1.80	0.13	330	1.65	0.44
	75	200	1.38	.19	250	1.65	.14	240	1.92	.20	300	1.65	.31
	135	245	1.55	.20	330	1.60	.17	280	1.81	.28	180	1.70	.52
	210	240	1.44	.32	275	1.70	.24	215	1.93	.26	220	1.55	.46
Dry gelatin added after washing, 60 per cent of original amount-----	60	76	1.30	.22	126	1.37	.18	230	1.48	.22	210	1.13	.65
	135	100	1.10	.35	140	1.30	.29	175	1.44	.41	220	.97	.63
	200	102	1.10	.41	140	1.26	.35	105	1.53	.48	120	1.16	.68

TABLE 38.—*Storage ripening of emulsions made by formula “A”*

[1 per cent AgI, and washed by centrifuge. All data are for 6 minutes development]

Emulsion No. and gelatin	Time of digestion	Time of ripening	Directly after coating			After 1 month storage			After 3 months’ storage ¹			After 13 months’ storage ²		
			Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog
8-101, Winterthur, untreated-----	Minutes at 45° 10	Minutes at 45° 6	12	1.46	0.08	36	2.30	0.05	66	2.30	0.14	72	2.14	0.34
		35	16	1.15	.26	47	1.50	.21	145	1.60	.29	132	1.60	.35
		63	34	.67	.32	138	.90	.28	350	1.08	.28	265	1.12	.48
		120	43	.50	.52	182	.67	.48	480	1.76	.52	350	1.15	.58
8-100, Winterthur, untreated-----	135	5	51	1.45	.13	43	1.70	.15	48	1.55	.12	30	1.70	.28
		30	135	1.05	.26	100	1.32	.24	110	1.31	.31	72	1.15	.42
		62	118	1.03	.46	175	1.10	.39	125	1.10	.49	200	.90	.64
		135	200	.87	.41	200	1.00	.46	210	.95	.45	240	.95	.55
8-108, Winterthur, digested with NH ₃ and washed-----	145	7	20	1.63	.11	25	1.85	.13	43	1.60	.15	95	1.55	.14
		29	31	.97	.22	45	1.00	.24	79	1.10	.25	190	1.05	.23
		59	39	.53	.30	39	.68	.31	180	.65	.28	315	.77	.30
		120	50	.34	.33	91	.38	.41	290	.58	.41	550	.68	.38

¹ 4 months’ storage of 8-108.

² 12 months’ storage of 8-108.

³ Approximately.

After-ripening by storage and by digestion are equally dependent on the gelatin. The ammonia-treated gelatins have a peculiarity which was indicated in Table 27 and is more evident in Table 38, emulsion 8-108; there may be little after-ripening over a considerable time of digestion or storage, followed ultimately by a great rise

of sensitivity. In emulsion 4-69, the after-ripening in the last 90 minutes of digestion was greater than in the first 90; in emulsion 8-108, storage for a year produced clean plates of unusually high speed numbers, although the contrast was still below normal. The obvious interpretation of this is that the more labile sensitizing materials were removed by the ammonia treatment but that a considerable amount of slowly reacting sensitizers was left.

The very important question of the effect of soluble bromide on storage ripening and deterioration by fog will be taken up in a later communication, as plates now in storage are expected to furnish data which should be included.

The processes occurring in storage ripening would be expected to be essentially the same as in after-ripening by digestion. The amounts of silver plus silver sulphide, as found by the Weigert and Lühr method (Pt. V of this paper), support this expectation. The only explanation which we can offer for the greater effectiveness of storage ripening has already been given on page 233, that in the slow process of storage ripening there is relatively little tendency toward the formation of new nuclei. It is therefore a process of growth of small numbers of nuclei per grain, leading to the most efficient utilization of the silver and silver sulphide formed, and also leading to rapid increase in fog when the nuclei increase past the optimum size. If the emulsion has previously been digested to maximum speed, this may have resulted in greater numbers of nuclei than if it had been subject only to storage ripening, with the further possibility that a higher proportion of the silver sulphide (or silver) particles have been formed by reaction with dissolved silver halide. These last may be independent of silver halide grains and, therefore, inert both as to sensitivity and fog. The supply of sensitizers has been partly exhausted, so that storage ripening in this case proceeds with a lowered rate of formation of silver and silver sulphide, distributed among a larger number of nuclei, some of which are ineffective; increase of any of the nuclei to the size causing fog is therefore retarded.

V. ANALYTICAL EVIDENCE ON THE MECHANISM OF AFTER-RIPENING

Digestion of silver bromide with gelatin may be expected to result in some reduction to metal. The analysis of the emulsion gelatins used in this investigation, by the method of Sheppard and Hudson (26), gives results of the order of 2×10^{-5} g. labile sulphur per gram of gelatin, at least part of which may react under the conditions of after-ripening. The total fraction of silver bromide converted to other (nonhalide) forms will, however, be very small. The available evidence on the photolysis of silver bromide indicated that the silver of the latent image corresponding to ordinary exposures was less than could be detected by any analytical method. As it was assumed that the ripening nuclei must be a much smaller quantity, it was not until Weigert and Lühr (27) extended their investigations of photolysis from "print-out" to "developing-out" emulsions that there was any attempt to determine the "ripening silver" by chemical analysis. In a forthcoming paper we will describe experiments with the Weigert and Lühr method in full detail; in the discussion of the connection

between after-ripening and nonhalide ("ripening") silver, the analytical results may be taken roughly at their face value.

Reduction or other reaction of the silver bromide during digestion could also be detected by an increase in the bromide ion concentration, when it was sufficiently low.

A number of typical results are given in Table 39. It will be noted that the rate of increase at a given temperature is greater for the emulsions with the lower proportions of iodide. It is less in the emulsion made with the deashed gelatin than the corresponding one with normal gelatin. Both these differences would be predicted, since increase in proportion of iodide makes reduction more difficult, and the deashing process probably removes reducing materials. The amount of silver bromide reacting can not be calculated from the change in bromide ion concentration, since there is not only the change in free silver and bromide ions, but a larger one in silver ion combined with the gelatin, and probably another of similar magnitude in bromide ion absorbed to the silver bromide. The errors in determination of these are too large to make the computation of any value.

Table 40 gives the results, both of digestion and of storage ripening, on the nonhalide silver, and photographic properties, of two emulsions. The increase produced by either digestion or storage ripening is much larger than the variations in the silver determinations; the values for each of the latter are given separately to indicate the reproducibility. It is evident that the increase in silver is more rapid at lower bromide ion concentrations, which is according to prediction, although, at 45°, increase in the bromide ion concentration by a factor of 40 divides the rate by 4 only, and at 55° by less than this. The rate of increase at 55°, without added bromide, is between two and three times as great as under the corresponding conditions at 45°, which is the normal value for a chemical reaction. The increase in nonhalide silver on storage was of the same order as that on digestion to a corresponding speed, and the effect of soluble bromide was very similar. On storage of 4-64-1 and 6, the increase in nonhalide silver, expressed in parts per 100,000, was 3.5 and 2.7; in 4-64-7, with no added bromide, the increase was 7.4. In emulsion 4-66, the corresponding values are 9.1 and 9.5 with added bromide, 18.2 without it. The difference between the two emulsions is unexplained. The data for digestion of emulsion 4-59, Table 41, are quite similar to those for 4-64 and 4-66.

TABLE 39.—*Change in bromide ion concentration of emulsions during digestion*

[Photographic data on these emulsions will be found in Tables 9, 10, 11, 12, 14, and 231]

Emulsion No.	Gelatin	Mol per cent AgI	pH	Time of digestion	Temperature of digestion, °C.	Bromide ion concentration at beginning of digestion, normality	Bromide ion concentration at end of digestion, normality
4-47	Winterthur	0.0	6.6	1.0	54	1.43×10^{-5}	1.92×10^{-5}
4-64	Winterthur-Nelson No. 1	1.0	6.9	4.0	45	1.8×10^{-5}	2.5×10^{-5}
4-66	do	1.0	7.0	2.0	55	1.5×10^{-5}	3.8×10^{-5}
1-162	Winterthur	1.0	8.3	3.0	45	1.75×10^{-5}	2.25×10^{-5}
4-61	Winterthur-Nelson No. 1	4.0	6.9	2.3	55	1.5×10^{-5}	2.7×10^{-5}
4-67	Deashed, from limed stock	4.0	7.1	3.0	55	1.42×10^{-5}	2.20×10^{-5}
1-159	Nelson No. 1	5.0	8.3	3.0	45	3.3×10^{-6}	5.8×10^{-6}

TABLE 40.—Effect of digestion and storage on photographic properties and nonhalide silver (determined by the modified Weigert and Lühr method)

[Emulsions made by "C" formula, 1 per cent AgI, 12.5 per cent excess NH₄Br, Winterthur and Nelson gelatin; mixed in 26 minutes at 52°]

Emulsion No.	Bromide ion concentration during digestion N	Time of digestion (minutes) and temperature	Directly after coating				Three months after coating			
			Ratio Ag×10 ³ / AgBr	Speed	γ ₆	Fog ₆	Ratio Ag×10 ³ / AgBr	Speed	γ ₆	Fog ₆
4-64-1	7.6×10 ⁻⁴	<10	6.0, 5.6	34	0.55	0.04	9.3	125	1.03	0.04
4-64-6	7.6×10 ⁻⁴	245, 45°	8.6, 7.3	170	1.04	.09	10.7	190	1.37	.12
4-64-7	1.8×10 ⁻³	240, 45°	15.9, 15.3	215	1.55	.22	22.0	210	1.52	.34
4-66-5	1.2×10 ⁻³	<10	{ 4.4, 10.0 4.5, 4.2 }	39	.33	.00	13.5	134	.84	.03
4-66-8	1.2×10 ⁻³	120, 55°	12.5, 12.4	170	1.63	.14	22.0	130	1.53	.37
4-66-4	3.8×10 ⁻³	120, 55°	14.8, 15.1	162	1.60	.21	33.2	150	1.57	.32

TABLE 41.—Change in nonhalide silver on digestion

[See Tables 8 and 12 for photographic data on these emulsions]

Emulsion No.	Digestion time	Bromide ion concentration, normality	Nonhalide silver by Weigert and Lühr method Ag/AgBr×10 ³	Digestion temperature	pH
1-159-2	Minutes				
4	<10				
6	53				
7	110				
4-59-1	180				
7	<5				
8	135				
	190				
		3.3×10 ⁻⁶	{ 36.8, 28 17.6, 11.9 16.9, 12.7 13.2, 10.1 8.1, 9.8 14.3, 12.2 11.7, 11.6 }	45°	8.3
		1.2×10 ⁻³			
		3.3×10 ⁻⁴			

In the case of emulsion 1-159 we have an anomalous behavior which was also observed on a smaller scale in the early stages of digestion of other emulsions. More nonhalide silver was found in the undigested portion than in the others; except for the undigested portion, the differences are within the limits of error of analysis. We have no reason to suspect random errors of analysis in these cases. It is possible that conditions favor a considerable systematic error. However, it is significant that the portion of this same emulsion which was digested with added bromide decreased in fog during digestion, so that an actual decrease in the nonhalide silver appears to be a possibility.

Granting that the nonhalide silver is real and that its changes are in most cases to be predicted from the chemistry of the system, the correlation with photographic properties is hardly close enough to be useful. The quantity of nonhalide silver found by the Weigert and Lühr method is invariably too large to be ascribed only to sensitivity nuclei. Reference to Tables 29 to 31 shows the large photographic effects of 2 parts of nonhalide silver per 100,000, when introduced by use of efficient sensitizers. The minimum value by analysis in the insensitive and very clean 4-66-5 was 4 parts per 100,000, and it generally rose to 10 to 15 parts on digestion to maximum sensitivity. In the opinion of the writers, only a small part of this nonhalide silver functions as sensitivity nuclei; the rest is dispersed

through the gelatin, but not adsorbed to silver halide grains. The initial amounts in undigested emulsions may have been formed during ripening, but an equally plausible explanation is given by the presence of traces of colloidal silver in silver nitrate, unless exceptional precautions have been taken to prevent it. The increase in nonhalide silver during digestion must, to a large extent, represent reaction of "silver gelatinate" and free silver ions with reducing materials or labile sulphur, leading to a free particle of silver or silver sulphide, in contrast to the adsorbed sensitivity nuclei formed by rearrangement of a compound already adsorbed to the surface of a grain.

VI. SUMMARY

1. This paper is a survey of the changes taking place in a photographic emulsion after it has been washed, and of the effects of eight independent variables or groups of variables.
2. In studying the independent variables of the process, experiments have been repeated using emulsions of varying iodide content, with and without ammonia, and with different samples of gelatin.
3. The dependence of after-ripening by digestion on temperature, bromide ion concentration and hydrogen ion concentration indicates that it is the result of a chemical reaction or reactions of the silver halide. Chemical analysis shows an increase in nonhalide silver roughly parallel to the photographic changes but in quantity too large to be explained as sensitivity nuclei only.
4. Experiments on after-ripening in inert gelatin plus known sensitizing materials (allyl thiocarbamide, sodium thiosulphate) gave results qualitatively very similar to those in active gelatin, although the characteristics of active gelatin can not be explained by allyl thiocarbamide alone.
5. If digestion after washing is omitted, there is a slow after-ripening on storage, with effects generally similar to those of digestion.

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